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# Appearance of surface magnetic moments on vanadium thin films and sensitivity to contamination

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Photoelectron spectroscopy with use of synchrotron radiation shows the appearance of satellite structure in the 3*s* core-level spectra of freshly evaporated vanadium films on graphite. The structure is more prominent relative to the main 3*s* peak in islanded films, from which a greater proportion of the signal is from the surface and the features are interpreted as due to 3*s* electrons from multiplet split core levels in surface atoms possessing a magnetic moment. The weaker $^3S$ component rapidly fades in an ambient pressure of $2\times10^{-11}$ mbar, showing that the magnetic moment is extremely sensitive to contamination. This may help to resolve the recent controversy surrounding the existence of surface magnetic moments on vanadium.

## INTRODUCTION

One of the exciting aspects of surface science is the discovery of unexpected magnetic behavior at surfaces and in ultrathin films. Of special interest is the search for magnetic order at surfaces, in ultrathin films and superlattices of metals which are paramagnetic in the bulk. The history of this search in the case of vanadium goes back to 1977 when Akoh and Tasaki measured a Curie-law dependence of the magnetization in ultrasmall particles.[1] The behavior of the susceptibility as a function of particle size led them to suggest the existence of magnetic moments localized on surface atoms. In 1979 Allen[2] showed that the condition for surface magnetism in paramagnetic metals is satisfied at the V(100) surface and the following year Grempel and Ying[3] predicted that the V(100) surface is antiferromagnetic with a Néel temperature of 3.8 K. More recent theoretical work has not been in accord with these early results, with Ohnishi *et al.*[4] and Freeman and Fu[5] predicting a paramagnetic state for the (100) surface of vanadium.

Calculations for the surfaces of ultrathin films all predict magnetic order.[6–9] Gay and Richter[6] showed that an isolated V(100) monolayer (with the silver lattice constant) is ferromagnetic with a local moment of $3\mu_B$ per atom. Fu *et al.*[7] predict a ferromagnetic alignment for vanadium monolayers on Ag(100) and Au(100) with local moments $1.98\mu_B$ and $1.75\mu_B$, respectively, and in the case of a bilayer $1.15\mu_B$ in the surface layer and $<0.05\mu_B$ in the interface layer. Blügel *et al.*[8] indicate antiferromagnetic order in a vanadium monolayer on Pd(100) with a local moment of $1.39\mu_B$. Yokoyama *et al.*[9] calculated the magnetic polarization at the surface of an isolated 5 monolayer (100) film of vanadium to be $0.2\mu_B$ per atom. Thus there is consensus among the calculations for ultrathin films on the existence of magnetic order in the topmost layer though disagreement remains about the type of spin alignment and on the magnitude of the polarization.

Since the work of Akoh and Tasaki, six experimental studies have been reported.[10–15] Electron capture spectroscopy (ECS) measurements by Rau *et al.*[10] show ferromagnetic order in the topmost layer of a V(100) crystal with a surface Curie temperature of 540 K. The same group[11] found magnetic order at the surface of ultrathin films of vanadium on Ag(100) up to a thickness of 7 monolayers. Moodera and Meservey[12] used surface impedance measurements to study the magnetic properties of vanadium deposited on Ag, Pb, Au, and Al substrates. Their general conclusion is that there is an antiferromagnetic coupling between vanadium atoms for coverages in the range 0.03 to 1.5 monolayers with a ferromagnetic layer formed at about 1.5 monolayers. Magnetic order is also indicated in the inverse photoemission measurements reported by Drube and Himpsel[13] for vanadium monolayers on Ag(111). In contrast spin-polarized photoemission[14] and surface magneto-optical Kerr effect[15] experiments show no evidence for magnetic order in vanadium monolayers on Ag(100).

Disagreement between different experiments on similar systems such as that between Refs. 14 and 15 and Ref. 11 indicate a factor not being accounted for such as contamination. This, as a possible source of discrepancy, has been suggested by the ECS measurements of Rau *et al.*,[11] who measure a significant reduction in the spin polarization in vanadium on Ag(100) on adsorption of 0.06 monolayers of oxygen. We report here core-level and valence-band photoemission measurements using synchrotron radiation of vanadium films on graphite. Our results indicate surface magnetic moments in freshly deposited layers which are quenched after exposures of less than 1 L of CO.

## EXPERIMENT

The experiment was carried out on beamline 6.1 of the synchrotron radiation source (SRS) at Daresbury laboratory, UK. Vanadium films were deposited onto HOPG from a compact electron beam source[16] in which the evaporant and filament are surrounded, apart from a 5 mm collimator, by a shroud through which was circulated a chilled water-antifreeze mixture. After thorough degassing it was possible to evaporate films with the chamber pressure maintained below $8\times10^{-11}$ mbar dropping immediately after deposition to the x-ray limit of the ion gauge ($2\times10^{-11}$ mbar). The main constituent of the residual gas was CO. In the text to follow, all quoted gas exposures are upper limits since they are calculated assuming the pressure was $2\times10^{-11}$ mbar as measured on the ion gauge, but the actual pressures are almost certainly lower.

Photoemission measurements were carried out on two samples, that is, a continuous film and an islanded film in which the average particle size was 5.98 nm. This was determined by a previously reported technique[17] which involves measuring the spectral dependence of the soft-x-ray reflectivity of the sample over the usable range of the monochromator (35–200 eV). Photoelectron spectra were recorded using a VSW HA 100 hemispherical analyzer employing 16 detection channels. The combined analyzer and monochromator resolution was 1.2 eV.

Substrates were cleaved in air and prior to deposition were heated in UHV to 800° C for 30 min. After deposition of vanadium, the sample cleanliness was checked using photoemission which is very sensitive to CO contamination. Figure 1 shows valence-band photoemission spectra taken using a photon energy of 120 eV as a function of exposure to the residual atmosphere in the UHV chamber (mainly CO). The feature at 6 eV binding energy is due to the CO $5\sigma/1\pi$ state and is detectable for exposures $\leq 0.1$ L. We can find no published data regarding CO coverage on vanadium versus exposure but for CO on Cr(110),[18] 0.1 L exposure results in a coverage of about 0.025 monolayers measured relative to the standard CO layer density. The absence of the $4\sigma$ photoemission feature is probably due to the "lying down" orientation of the molecules as observed for low coverages on Cr(110).

## RESULTS AND DISCUSSION

Figure 2 shows photoemission spectra of the vanadium 3*s* core level taken with a photon energy of 140 eV from the freshly evaporated continuous and islanded films. There is no detectable contamination in the valence-band spectrum from the particles whereas the thick film shows a CO $5\sigma$ and $1\pi$ peak whose intensity corresponds to an exposure of about 0.2 L. The results to be presented show that this is too low to significantly affect the 3*s* spectrum. In both curves a satellite is visible 6 eV below the bulk 3*s* feature, which we ascribe to the $^3S$ component of a multiplet split 3*s* feature from surface atoms possessing a magnetic moment. We would expect a greater surface signal relative to the bulk from the islanded film, and for island sizes significantly greater than the photoelectron escape depth (as is the case here), the surface enhancement is about a factor of two. Thus the $^3S$ com-

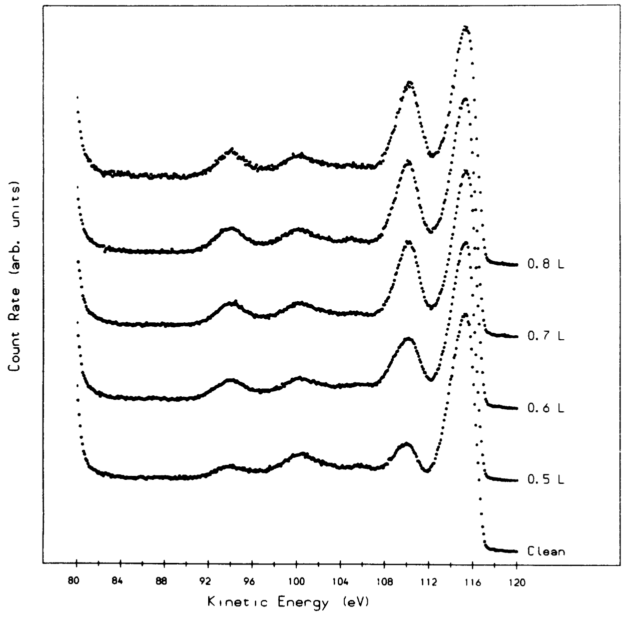

FIG. 1. Valence-band photoemission spectra taken with a photon energy $h\nu=120$ eV as a function of exposure to the residual gas in the vacuum chamber at a pressure of $2\times10^{-11}$ mbar.

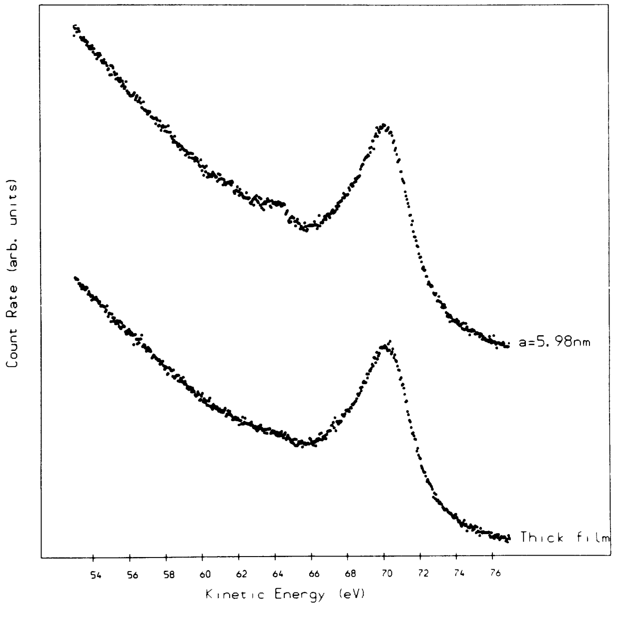

FIG. 2. 3*s* core-level photoemission spectra taken with a photon energy $h\nu=140$ eV from continuous and islanded vanadium films.

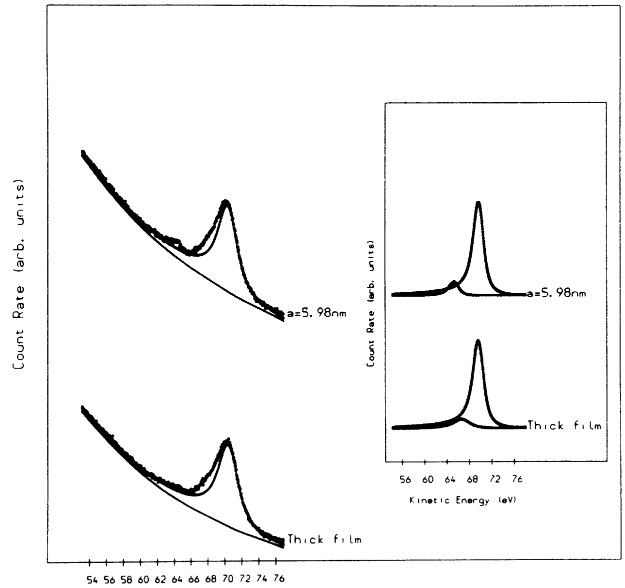

FIG. 3. Raw data (circles) plotted with fitted background and background plus bulk 3*s* peak (lines) as determined by the Doniac-Šunjić fitting routine. Inset: Fitted surface 3*s* peaks $^3S$ and $^5S$ components.

ponent (6 eV satellite) is observed to be more prominent in the spectrum from the particles. This peak cannot be due to contamination, as none was detected, and allowing the sample to contaminate in the vacuum chamber environment results in a reduction in its intensity and the appearance of a new satellite 8.3 eV below the main 3*s* peak (Fig. 4). The larger $^5S$ component is unresolved from the bulk 3*s* feature though a weak shoulder can be made out on the high binding energy in the case of the thick film. An alternative explanation for the 6 eV satellite is that it is due to the entire unsplit 3*s* feature from surface atoms with no magnetic moment. We reject this, however, since its intensity relative to the main peak implies an unreasonably long scattering length for the 3*s* photoelectrons.

To obtain more information, the 3*s* data were fitted to model spectra containing three peaks with a Doniach-Šunjić[19] line shape convoluted with Gaussians of width 1.2 eV. The background was included as part of the minimization and was modeled by a Tougaard[20] contribution with no adjustable parameters for the scattered primaries and a fourth-order polynomial for the secondary tail. In order to reduce the number of parameters in the minimization, this background was first fitted to either side of the primary features and then introduced into the fitting routine with two adjustable parameters allowing a vertical stretch and an overall shift of the curve. The program used has been developed over a number of years and has been found to be extremely reliable in a wide variety of applications.

The results of the fit are shown in Fig. 3, which presents the raw data along with the fitted background and main 3*s* peak. The inset shows the multiplet split surface 3*s* components showing multiplet splittings of 3 and 4.4 eV for the continuous and islanded films, respectively. The intensity ratio of the $^3S$ and $^5S$ peaks is about the same ($\approx 1{:}6$) in both samples.

Figure 4 shows a series of spectra from the islanded film taken as a function of time elapsed in the residual atmosphere in the UHV chamber with upper limit exposure values indicated. The raw spectra show an overall decrease in the intensity of the $^3S$ surface component and a corresponding increase in a satellite 8.3 eV below the main 3*s* peak. This feature is clearly associated with the buildup of CO contamination observed in the valence-

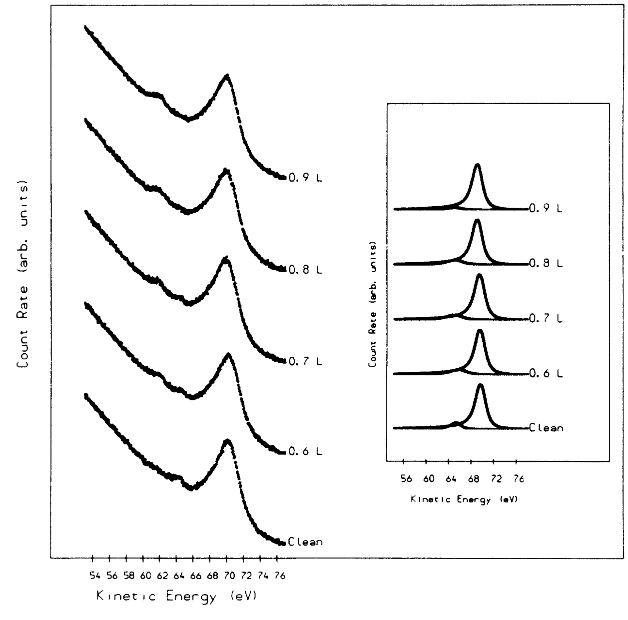

FIG. 4. 3*s* core-level photoemission spectra taken with a photon energy $h\nu = 140$ eV as a function of exposure.

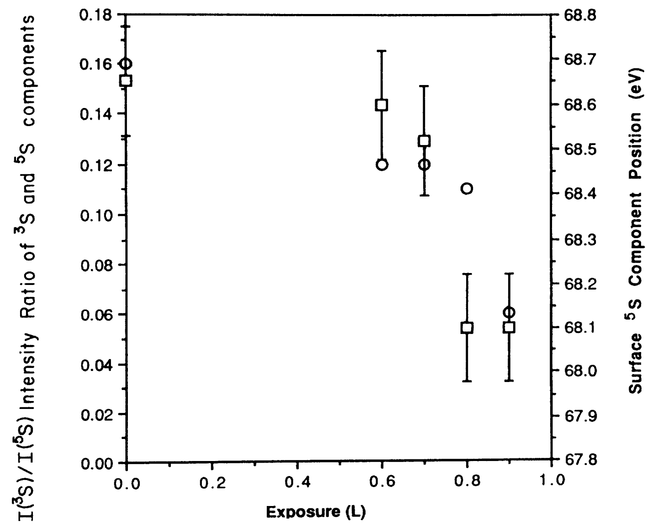

FIG. 5. Intensity ratio of surface 3*s* peak $^3S$ and $^5S$ components as a function of exposure (○). Position of surface 3*s* peak $^5S$ component as a function of exposure (□).

band spectra but its precise origin is unclear. These spectra have been analyzed with the fitting routine after including a fourth Doniach-Šunjić component to model the contamination peak. The results for the surface 3*s* component are shown in the inset and the intensity ratio of the peaks and the kinetic energy of the $^5S$ component plotted in Fig. 5. The disappearance of the $^3S$ component is accompanied by a shift in the $^5S$ peak to the center of gravity of the two features observed in the clean spectrum. The conclusion is that CO contamination causes a reduction of the surface moment leading to complete quenching after an upper limit exposure of about 1 L. Bearing in mind that this is the exposure received in 3 h at a pressure of $1\times10^{-10}$ mbar and that the exposure figures quoted here are probably a significant overestimate, these results could well explain the discrepancy between different experiments described in the Introduction.

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