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LETTER TO THE EDITOR

Photoemission intensity variations from the quantum well state in the Ag/V(100) single-monolayer overlayer structureD P Woodruff[†], M Milun[‡] and P Pervan[‡][†] Department of Physics, University of Warwick, Coventry CV4 7AL, UK[‡] Institute of Physics, PO Box 304, 10000 Zagreb, Croatia

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Abstract. Normal-emission photoemission spectra from the quantum well state in a single monolayer of Ag on V(100) have been studied as a function of photon energy. By comparing the measured binding energy and calculated electron momentum perpendicular to the surface in this state with the unoccupied s–p bands of Ag and V, we show that the peak intensity corresponds to the condition expected for a direct transition in V(100). This result is consistent with the fact that the state is in many ways similar to an intrinsic Shockley surface state of a clean surface.

The existence of quantum well (QW) states in thin metal films on metal substrates is now well established, and in the case of noble metal/transition metal layers and multilayers, these states have been implicated in the magnetic coupling which can lead to giant magnetoresistance in these films [1, 2]. Occupied QW states have been characterized by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), but as yet little attention in these studies has been focused on the importance of the choice of photon energy. It has been suggested that the QW states should exhibit peak photoemission intensities at photon energies corresponding to direct transitions from extended states at the same binding energy in bulk material having the same structure as the overlayer film [3]. While this must clearly be true for sufficiently thick films (in the limit in which they become bulk crystals), there seems little reason to believe that this will be appropriate for very thin films. Indeed, the limiting thin-film case is that of a quantum well state having an associated wavefunction with no nodal planes parallel to the surface (as can occur in single-monolayer films, in particular). In this case the wavefunction is far more like that associated with an intrinsic Shockley surface state of a clean surface.

In several examples studied in the past [4, 5] the photoemission intensity from specific Shockley surface states has been found to peak at the photon energy which produces the direct transition from the bulk s–p band state closest in energy to that of the surface state. This has been ascribed [4, 5] to the fact that the exponential tail of the surface-state wavefunction in the outermost layers of the solid will show oscillations which will define a dominant Fourier component, and the period of this oscillation will be close to that of the states of the bulk bands at the gap edge. An implicit requirement in this description, of course, is that either the initial- or final-state (or both) electrons sample enough of the periodic potential of the substrate perpendicular to the surface to acquire the substrate reciprocal-lattice vector required to ensure momentum conservation implicit in the direct-transition picture. Notice that if this description were to be appropriate for a QW state of a single-monolayer overlayer, it would imply that the

final state defining the ‘direct transition’ is to be found in the band structure of the *substrate*, not the overlayer material.

As part of a more extensive study of the photon energy dependence of photoemission from QW states in ultra-thin (1–7 monolayer) epitaxial films of Ag on V(100), we have found clear evidence for this effect. We present, in particular, results for photoemission from a QW state in a single monolayer (1 ML) of Ag on V(100) which is known to have no internal nodal planes parallel to the surface.

QW states in the Ag/V(100) system have been previously investigated using fixed-energy laboratory-based photon sources [6], while the characteristics of the overlayer growth have also been described elsewhere [6–8]. Briefly, at room temperature, silver grows pseudomorphically in an ordered layer-by-layer mode when deposited onto an ordered and clean V(100) surface whose electronic structure is characterized by an s–p band gap extending 2 eV above and below the Fermi level, E_F , along the Δ_1 high-symmetry directions. This growth mode is preserved for at least ten atomic layers. Above room temperature, the Stranski–Krastanov growth mode prevails, with two pseudomorphic silver monolayers serving as a substrate for Ag clusters. Above 900 K, silver desorbs from the V(100) surface. Annealing at 800 K of any silver film thicker than 0.5 ML deposited on an oxygen-contaminated V(100) surface produces a clean and very well ordered substrate and film, as is evident from Auger electron spectroscopy, x-ray and ultraviolet photoemission spectroscopy, work-function measurements and low-energy electron diffraction [9]. In this way it is possible to produce a well ordered and clean V(100) surface covered with an ordered silver film of up to 2 ML coverage.

The measurements were performed at the toroidal grating monochromator beamline (6.2) on the Synchrotron Radiation Source (SRS) of the Council for the Central Laboratories of the Research Councils (CCLRC) at Daresbury Laboratory. The end-station was equipped with an ARUPS facility based on a movable 50 mm hemispherical analyser (VG ADES 400). The light was incident on the V(100) crystal surface at an angle of 40° to the surface normal, while the analyser was set to collect electrons emitted at normal emission. The typical angular acceptance angle of the analyser was 1.5° and the energy resolution of 200 meV was maintained throughout the experiment. The measured intensities were normalized with respect to the incident photon beam intensity monitor.

Figure 1(a) shows a normal-emission photoelectron energy spectrum recorded from a 1 ML film of Ag on V(100). Three peaks dominate the spectrum: the intense peak from a state 1.6 eV below the Fermi level attributed to the QW state in this system, and two peaks at 5.1 and 6.2 eV assigned to the silver 4d electrons. A small peak at 0.3 eV is assigned to the vanadium 3d valence band. The Ag 4d part of the spectrum differs substantially from that found for bulk silver as might be expected. The narrow two-peak lineshape suggests an atomic-like character. However, the separation of the two peaks (1.1 eV) is much larger than the 4d spin–orbit splitting in free Ag atoms (0.6 eV) and further photoemission spectra taken at different emission angles show that these peaks do disperse, clearly implying the formation of a two-dimensional band. Note, however, that the structural model of the 1 ML film shown [8] in figure 1(b), in which the silver-atom layer follows the structure of the underlying V(100) surface, leads to an Ag–Ag atomic separation 0.13 Å greater than in bulk fcc silver, so even in this monolayer, reduced Ag–Ag hybridization can be expected.

Despite this reduced intra-layer interaction, the presence of the QW state shows that the s–p electrons form an electronic system which is delocalized parallel to the surface but highly localized and quantized perpendicular to the surface. The energy of this QW state has been successfully matched [6] using the phase accumulation model [10, 11] which also provides a value for its associated electron momentum perpendicular to the surface, k_\perp , inside the well of 1.00 \AA^{-1} . Nevertheless, the QW state is not truly free-electron-like. Its experimentally

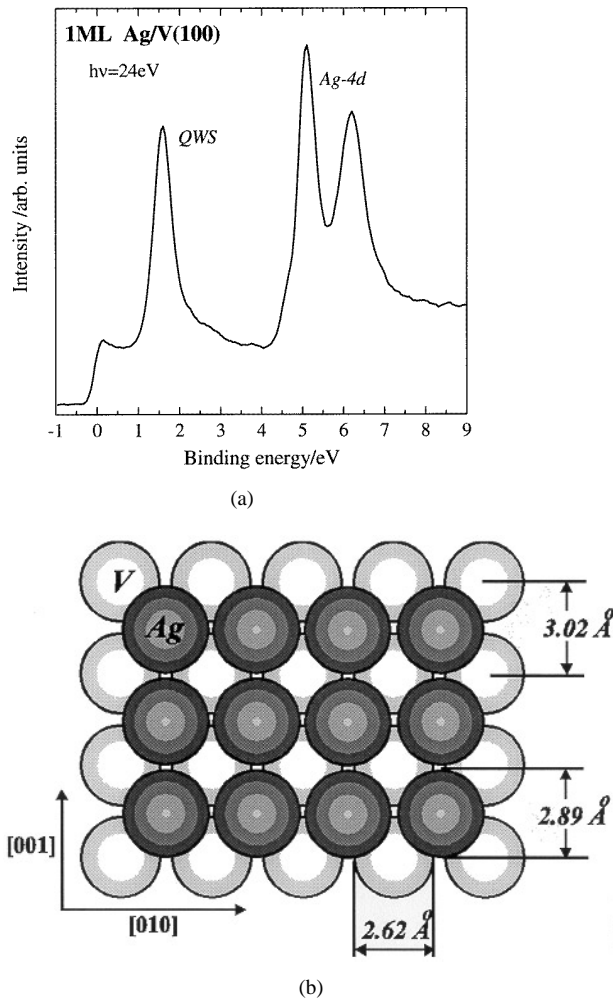
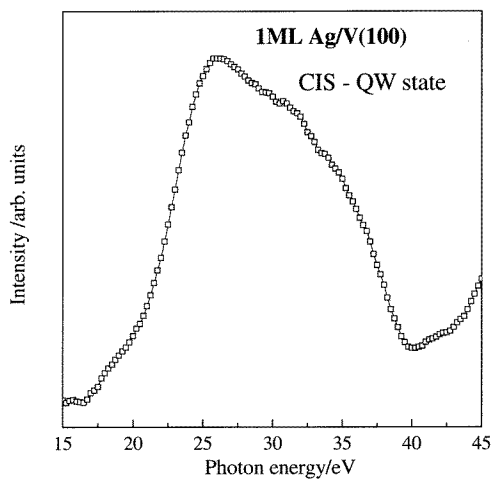


Figure 1. (a) The normal-emission photoemission spectrum recorded from a V(100) surface covered with a 1 ML Ag pseudomorphic overlayer at a photon energy of 24 eV. (b) A schematic plan view of the 1 ML Ag/V(100) surface, the Ag and V atoms being shown as spheres having sizes corresponding to their metallic radii in bulk V and Ag respectively.

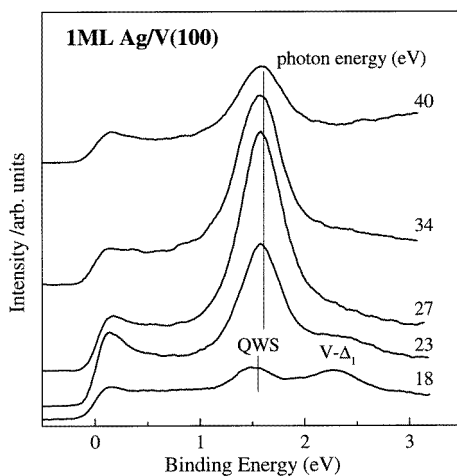
determined dispersion has been shown [6] to be consistent with an effective electron mass of $2.2 m_e$ and ascribed [6] to coupling to the vanadium 3d bands located within the same binding energy range.

Figure 2(a) shows the photon energy dependence of the intensity of this QW state in the photon energy range from 15 eV to 45 eV and figure 2(b) shows several individual photoemission spectra taken at selected photon energies. Clearly photoemission from this state is strongly dependent on photon energy, the broad peak and low-intensity minima being rather similar to previously published surface-state data, although in the present case the peak appears to have two or more components. One possible reason for this, as described above, is the influence of direct transitions into unoccupied final states of the V(100) substrate.

In order to test this idea one needs to know the form of the band structure of V(100) along its surface normal up to about 45 eV above the Fermi level, but most published band



(a)



(b)

Figure 2. (a) The constant initial state (CIS) showing the photon energy dependence of the photoemission signal from the QW state of the 1 ML Ag/V(100) surface in the 15–45 eV photon energy range. (b) Normal-emission photoemission spectra recorded from the 1 ML Ag/V(100) surface at several different photon energies.

structures are truncated a few eV above E_F . We have therefore obtained approximate band structures from a multiple-scattering muffin-tin potential model contained in the PHOTON computer code used for calculating photoemission spectra, based on the original formulation of Pendry [12]. The results are shown in figure 3. The superimposed lines indicate direct transitions from the QW state at the previously derived k_{\perp} -value. Notice that only final states of Δ_1 symmetry are allowed, and the symmetries of the lower bands are labelled on the basis of previous assignments in related calculations. The lowest appropriate Δ_1 -band final-state energy (ignoring the state at only 3 eV above E_F which is thus below the vacuum level) for a direct transition is approximately 23 eV, implying a photon energy of approximately 25 eV. Higher-energy final states occur around 35 eV. These can thus account rather well for

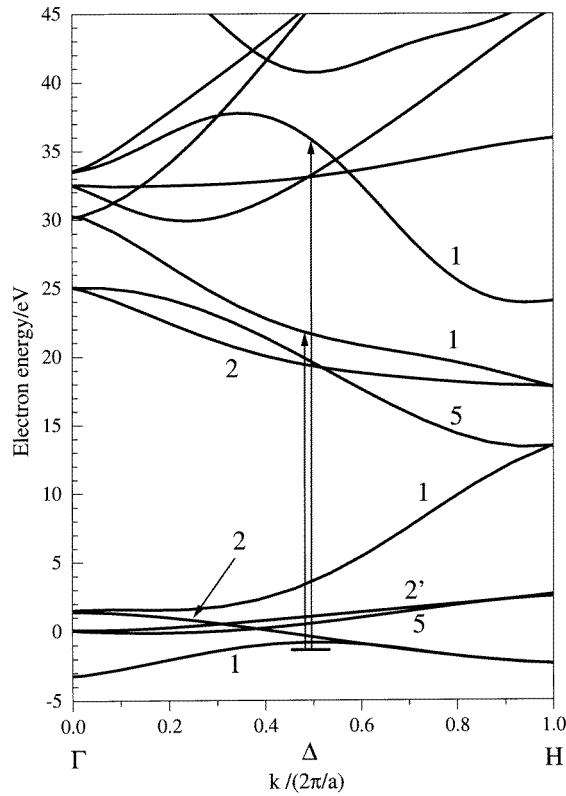


Figure 3. The calculated vanadium band structure along the [100] direction as described in the text. The superimposed lines indicate possible direct transitions from the QW state at its previously derived k_{\perp} -value.

the split-peak character of the QW photoemission intensity peak in this photon energy range (figure 2(a)).

We should note that this successful matching to the conditions for a direct transition to a V(100) final-state band contrasts strongly with the situation if we assume that the appropriate final state is described by the Ag(100) band structure; in this case the first direct transition is predicted to occur at a photon energy around 15 eV, and indeed thick Ag films do show an s-p band peak dispersing through the energy corresponding to the binding energy of the 1 ML QW state at this photon energy. By contrast, figure 2(a) shows that this photon energy corresponds to a minimum in the QW photoemission intensity. As a single monolayer of Ag clearly cannot be expected to show a bulk Ag band structure perpendicular to the surface, this failure is scarcely surprising.

In summary, we set out to answer two key questions; how important is the conservation of momentum perpendicular to the surface in QW photoemission and, if it is important, what is the origin of the reciprocal-lattice vector leading to it? For the 1 ML Ag film on the V(100) surface we see strong photon-energy-dependent intensity variations in the photoemission which can be reconciled with direct transitions to final states of bulk V(100). We therefore deduce that momentum conservation is important and that, as for an intrinsic surface state on a clean surface, it is satisfied by a reciprocal-lattice vector of the substrate. Notice, incidentally, that the initial k_{\perp} -value that we have used in our analysis is based solely on the multiple-reflection model

inside the quantum well, and takes no account of any possible oscillation of the evanescent tail of the associated wavefunction in the substrate. The implication is thus that the acquisition of the reciprocal-lattice vector for momentum conservation arises entirely from the substrate Bloch functions in the final state.

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