Interatomic Resonant Photoemission from Quantum-Well States in Ultrathin Films of Ag on V(100)

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Normal emission photoemission spectra from a single ordered monolayer of Ag on V(100) show a sharp and intense peak associated with a quantum-well state. The photon energy dependence of the intensity of this peak shows an identical enhancement profile to the V $3d$ photoemission in the vicinity of the V $3p \rightarrow 3d$ excitation threshold, characteristic of resonant photoemission. The significance of this result for resonant photoemission characterization of materials is discussed. [S0031-9007(98)07793-X]

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The phenomenon of resonant photoemission is now well established and has been observed in many materials [1]. In vanadium, for example, when the incident photon energy matches the threshold for photoexcitation of the $3p$ state to the unoccupied part of the $3d$ band, coherent interference can occur between the direct photoemission from the valence band and the autoionization involving this transition. In the simplest cases the effect leads to a characteristic Fano line shape in the resonance. Because the effect requires significant coupling to the localized core state resonant photoemission has been used in studies of valence band photoemission line shapes in a range of materials (e.g., [2–4]) to associate different parts of the valence band with the constituent elements. However, we here present evidence that *interatomic* resonance can occur in photoemission, calling into question the general reliability of this area of application.

The particular system we have studied is ultrathin epitaxial films of Ag grown on V(100). This growth system is extremely well characterized, and normal emission photoemission shows discrete quantum-well (QW) states localized in the Ag films in the binding energy range down to 2 eV below the Fermi level corresponding to the projected s-p Δ_1 band gap in the substrate [5]. Resonant photoemission from the valence band of V is well known to produce a broad peak in the photon energy range around 65 eV which appears above the V $3p \rightarrow 3d$ transition of approximately 37 eV [6]. We find, however, that the photoemission signal from the QW state in a single monolayer (ML) film of Ag on V(100) shows a photon energy dependence essentially identical to that of the V substrate, indicating the existence of an interatomic resonance in which the QW state must participate in the decay of the V $3p \rightarrow 3d$ excitation.

The decay of the excited state ($[3p^5 3d^{n+1}]^* \rightarrow 3p^6 3d^{n-1} + e$) is, of course, essentially equivalent to an Auger process except that in the normal Auger process the initial core excitation is into the continuum and the final state is a two-hole, rather than one-hole, state. Nevertheless, the requirements for interatomic resonant photoemission can be expected to be somewhat similar to those for interatomic Auger processes which have been known to occur for many years in conventional Auger electron spectroscopy [7]. The most common cases are in oxides (e.g., Ref. [7]) and alkali halides (e.g., Ref. [8]) in which the valence charge is largely localized on the oxygen or halogen anion, so if a shallow core hole is created on the metal cation the only decay mechanism is via the anion valence electrons. Interatomic Auger processes also form the dominant route for neutralization in low energy He^+ ion scattering from metals, the He^+ ion again having no shallower valence electrons to permit an intra-atomic Auger process (e.g., Ref. [9]) and forms the basis of the Knotek-Feibelman mechanism [10] of photon-stimulated desorption from oxide surfaces. It is therefore reasonable to anticipate that interatomic resonant photoemission may be possible in largely ionic materials. Indeed, Kay *et al.* [11] have reported very recently the observation of interatomic (or "multiatom") resonant photoemission in MnO and in two other oxides. Such a process would not previously have been expected, however, in a metallic system.

The experiments reported here were performed at Daresbury Laboratory using light from the Synchrotron Radiation Source at beamline 6.2 which is equipped with a torroidal grating monochromator covering the photon energy range 15–150 eV. The ultrahigh vacuum surface science end station was fitted with the usual sample handling, cleaning, and characterization facilities, and the methods used for cleaning the V(100) surface and preparing well-characterized Ag overlayer films have been described previously [5]. Photoemission electron energy spectra were collected using the VG Scientific ADES rotatable spherical-sector electron energy analyzer at normal emission using photons incident at 40° in the photon energy range 15 to 90 eV. A typical spectrum of this kind is shown in the inset of Fig. 1 taken from a 1 ML Ag film and shows a weak peak associated with emission from the V $3d$ band (close to the Fermi level), an intense peak from the QW state (which in this case has an associated wave function with the number of nodal planes parallel to the surface, $m = 0$) at a binding energy of 1.64 eV, and further structure from the Ag $4d$ electrons in the binding energy range 4–7 eV. Separate measurements of the intensities at the QW peak energy, and at a slightly higher kinetic energy to provide a background for subtraction from the QW intensity, were recorded in much smaller (0.25 eV) photon energy steps, and the resultant CIS (constant initial state) spectrum is shown in the main part of Fig. 1. For comparison an equivalent CIS spectrum recorded from the V(100) d-band on the clean surface is also shown.

It is clear that in the photon energy range of the V $3p$-$3d$ resonance the CIS spectra of the V d-band and QW state are almost identical. The selection of photoelectron energy spectra shown in Fig. 2 provides clear visual evidence of the strong enhancement of the QW peak intensity around the photon energy of 65 eV. Notice that the very broad double-peak line shape of the CIS seen in Fig. 1 is characteristic of this resonance in solid V as described in more detail elsewhere [6]. Separate measurements were also made of a series of other QW states, and we show in Fig. 3 a comparison of the photoemission intensity from the 1 ML ($m = 0$) QW and from two other states corresponding to 2 ML ($m = 1$) and to 4 ML ($m = 2$) (note that there is no occupied QW state for a 3 ML film). All of these CIS data show significant oscillations in their intensity, but only the 1 ML film shows the very strong enhancement in the region of the V $3p \rightarrow 3d$ resonance, the 4 ML film state showing no obvious enhancement which can be correlated with the resonance. Photoemission from the QW state of the 2 ML film does show significant enhancement of the intensity in the range of the V $3p$ resonance, but it is much less pronounced than for the 1 ML film.

Photoemission intensity oscillations from QW states can largely be understood in terms of a modification of the Adawi [12] description of surface photoemission, in this case involving coherent interference between emission from the film/vacuum (surface) interface and from the substrate/film interface. This idea has already been discussed by Carlsson *et al.* [13,14] in the context of their own work at very low photon energies on QW states in Na and Cs films on Cu(111). Our measurements on V(100)/Ag at film thicknesses from 1–7 ML are far more extensive, and fuller details of these results and their theoretical modeling will be presented elsewhere [15]. Typically, however, both

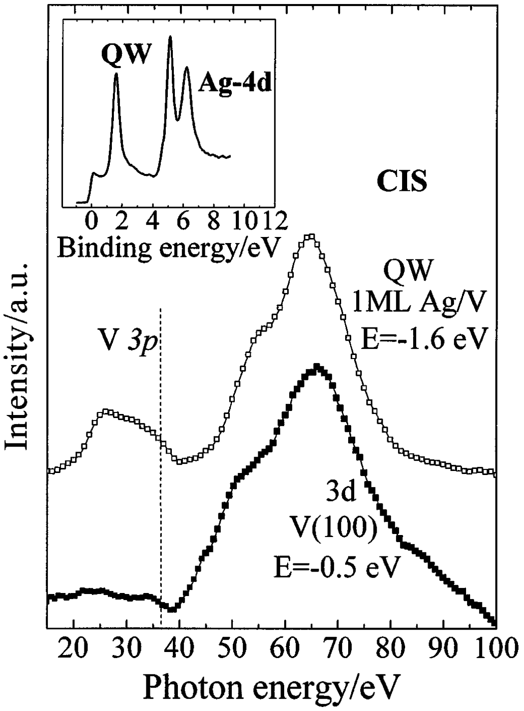

FIG. 1. Constant initial state (CIS) spectra showing the photon energy dependence of the photoemission intensity from the clean V(100) $3d$ band and from the QW peak of the spectrum recorded a 1 ML Ag film on V(100). The inset shows a typical photoelectron energy spectrum from the overlayer system.

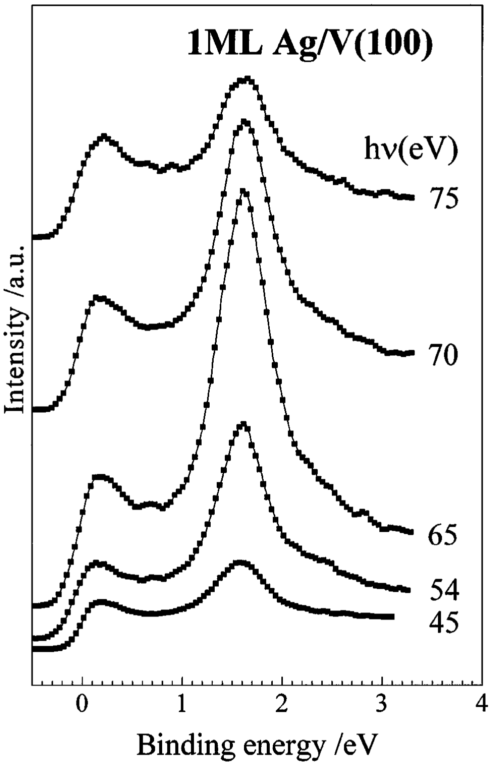

FIG. 2. Normal emission photoelectron energy spectra recorded at various photon energies from the 1 ML Ag film on V(100).

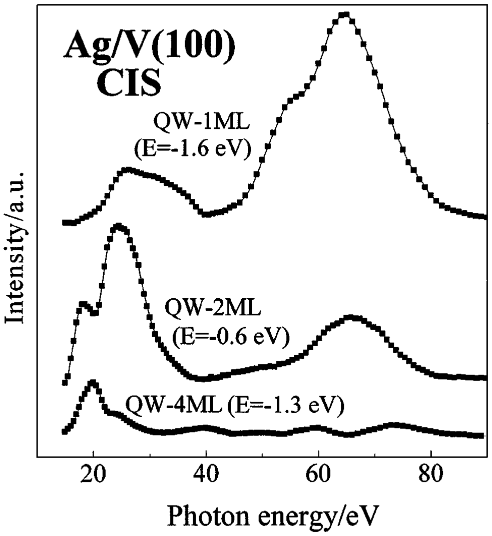

FIG. 3. Comparison of CIS spectra from the quantum-well states associated with 1, 2, and 4 ML of Ag on V(100) as described in the text.

our experimental results and our theoretical simulations show intensities above photon energies of about 40 eV to be much weaker than at lower energies. The very strong enhancement of the QW photoemission intensity seen from the 1 ML film for photon energies above 40 eV cannot be understood in these terms and must be associated with interatomic resonant photoemission.

As noted above, the most common situations in which conventional interatomic Auger processes have been seen is in systems in which Auger decay can proceed *only* by an interatomic process. This is clearly not the case here, and indeed we do see the resonance in the V $3d$ photoemission, even in the presence of the QW. Our observation must therefore rely on strong coupling of the QW overlayer state to the V $3d$ band. In this context the fact that we observe the effect strongly only for the thinnest, 1 ML Ag film, is reasonable. As the film thickness increases the renormalization of the single-electron wave function ensures that its amplitude at the substrate/film interface must fall with increasing thickness. We also note that the bcc (100) surface of V is very open on an atomic scale, and the first monolayer Ag atoms are thus embedded into the V surface, such that the Ag-Ag separation is significantly larger than in bulk Ag. Finally, we note that while the QW states occur in the V(100) Δ_1 band gap, and so cannot couple to the substrate s-p electrons, there is evidence of strong hybridization of the QW state with the V $3d$ electrons. In particular, we have shown that the dispersion of 1 ML QW state with parallel electron momentum implies a high effective mass ($2.2m_e$), most readily reconciled with $3d$ hybridization [5]. Moreover, tight-binding calculations for Ag on Fe(100) provide explicit evidence of this interaction on this related surface [16].

While these arguments make it possible to understand why this particular QW state is likely to couple relatively strongly to the underlying V $3d$ states, the clear implication of an interatomic Auger-like process contributing to resonant photoemission in a purely metallic system is surprising. It also has considerable potential ramifications. Resonant photoemission is extensively used as a means of characterizing the local origins of specific features in the valence bands of materials. This not only includes metallic alloys [2], but also oxides, such as band-gap states in titania [3] and cuprate superconductors [4]. The implicit assumption of such studies is that those parts of the valence band photoemission showing resonant behavior characteristic of one of the constituent elements originate from those atoms. If interatomic processes can be important, the whole basis of these studies is cast into doubt. One might, of course, question the extent to which the word "interatomic" is strictly valid in that the QW state is not localized on the Ag atoms although the charge density in the 1 ML ($m = 0$) QW state does peak in a plane centered on the Ag atoms. On the other hand, the QW state is certainly Ag induced, so the "atomic" part of this label is effectively the same as that used in the interpretation of resonant photoemission from alloys and compounds.

Of course, in questioning the significance of interatomic processes in the proper interpretation of resonant photoemission from complex materials a key issue is the magnitude of the effect; if interatomic processes are very much weaker than intra-atomic ones, they are unlikely to lead to gross misinterpretation. This question is especially germane to the recent observation of multiatom resonance (albeit in core level photoemission) in a mixed oxide showing colossal magnetroresistance [11]. In the present case, however, we see that the magnitude of the resonant enhancement of the photoemission from the 1 ML QW state is quantitatively identical to that from the V $3d$ state, so the implication would be that the QW is wholly V $3d$ in character. Calculations for the closely related Ag/Fe(100) system certainly do show the 1 ML QW to have significant substrate $3d$ character [16]; however, even for this state substantial s character is found, and these same calculations also show strong substrate $3d$ character in the QW states from 4 ML Ag films, whereas our data show no resonant enhancement in this case. This observation clearly indicates that substrate hybridization is not a sufficient condition for strong resonant enhancement, but is consistent with the idea that the proximity of the atom in which the core hole (V $3p$) is created is crucial, as has been proposed in the recent interpretation of multiatom resonant photoemission in oxides [11].

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