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Resonant electron emission in Ti and TiO_2

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A direct electronic recombination process is observed following $3p$ excitation in both Ti and TiO_2. In Ti this leads to resonant photoemission from the $3d$ valence levels at a photon energy 14 eV above the $3p$ threshold. In TiO_2 the oxide valence-band emission is enhanced at the $3p$ resonance energy. This is the first observation of interatomic resonant photoemission in an oxide. The resonant electron emission is also observed in electronically excited Auger spectra.

We report the first measurements of resonant electron emission far above the $3p$ excitation threshold in a transition metal using simultaneously resonant photoemission [ultraviolet photoemission spectroscopy (UPS)], electron-energy-loss spectroscopy (ELS), and electron excited Auger spectroscopy (AES), as well as a controlled change in the chemical environment (oxidation). Interatomic resonant photoemission is observed for the first time in the oxide [the only other example of an interatomic resonance being reported for KI (Ref. 1)]. It has been found that enhancement of $3d$ photoemission in Ti occurs at photon energies around 47 eV (i.e., 14 eV above the $3p$ threshold). In the maximum valency oxide TiO_2 the oxide valence-band (OVB) photoemission also resonantes at the same photon energy. The resonant photoemission indicates the existence of another deexcitation mechanism in addition to the normal super Coster-Kronig (SCK) Auger process. This second mechanism is a direct recombination-type process, where the energy of the excited $3p$ shell is transferred directly to a valence electron which is ejected with substantially higher kinetic energy than the Auger process would provide. The existence of this mechanism is also proved by Auger electron spectroscopy (AES).

In a (simplified) single electron picture the resonant emission can be described by a resonant excitation process $3p^6 3d^2 4s^2 \rightarrow 3p^5 3d^3 4s^2$ followed either by an autoionization process $3p^5 3d^3 4s^2 \rightarrow 3p^5 3d^2 4s^2 + \epsilon l$ (the kinetic energy ϵ being the same as in ordinary direct $3p$ photoemission. l defines the angular momentum of the outgoing electron with respect to the emitting atom) and subsequent SCK Auger decay $3p^5 3d^2 4s^2 \rightarrow 3p^6 4s^2 + \epsilon' l$ or followed by a direct recombination process $3p^5 3d^3 4s^2 \rightarrow 3p^6 3d^1 4s^2 + \epsilon'' l$.[2]

Resonant photoemission has been investigated extensively in Mn (Ref. 3) and Ni (e.g., Refs. 4–7). Only one report exists for Cr.[8] The direct recombination mechanism has been clearly demonstrated in atomic Mn.[3] In solid Cr a similar process has been postulated, although the details are not yet clear.[8] In the case of Ni, the controversy about the 6-eV satellite and the main band resonance enhancement is not yet resolved. In the solid metals Mn to Ni the resonance occurs right at the $3p$ absorption threshold. Therefore a quantitative assessment of the relative contribution of Auger and autoionization channels in the solid metals is difficult due to overlapping structures. Even angular distribution[9] and spin polarization measurements[10] on Ni satellite were not conclusive. In the case of Ti, however, the $3p$ excitation resonance occurs 14 eV above threshold. Therefore the Auger (ϵ') and the direct recombination (ϵ'') peaks are separated by 16 eV, as is shown in the present study.

The experiments were made in a stainless-steel UHV chamber at a base pressure of 2×10^{-10} Torr. ELS, AES, and UPS spectra have been measured with a double pass cylindrical mirror analyzer at a fixed pass energy of 15 eV. The SURF II synchrotron radiation source at the National Bureau of Standards (NBS) served as the photon source. The incident photon beam and analyzer axis were at an angle of 90° and both in the same plane with the surface normal and the polarization vector. Sample cleaning was performed by repeated Ar sputtering and heating cycles. Residual surface hydrogen could be removed by oxygen exposure and subsequent heating at 750 °C.

In Fig. 1 electron-excited Auger spectra of the

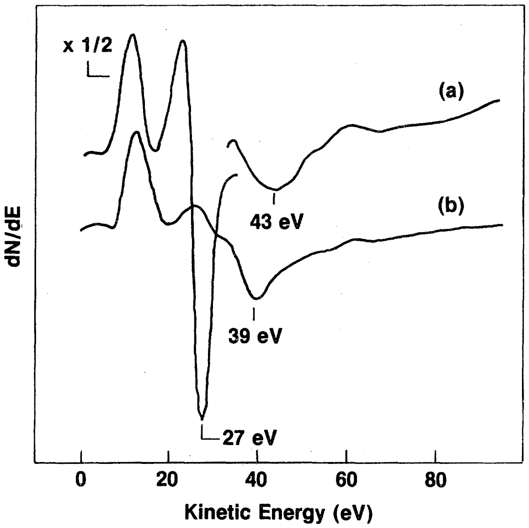

FIG. 1. Electron-excited $M_{23}VV$ Auger spectra of (a) Ti(0001) and (b) Ti(0001) + 48 L O_2.

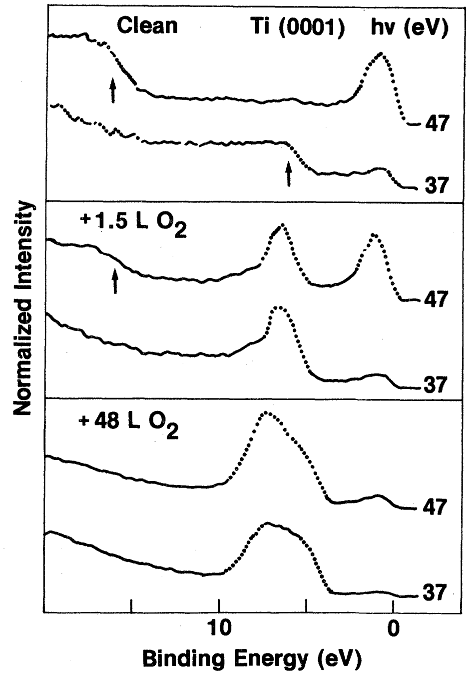

FIG. 2. UPS spectra of the valence-band region of clean and oxidized Ti(0001) on resonance ($h\nu=47$ eV) and off resonance ($h\nu=37$ eV). The arrows mark the $M_{23}VV$ Auger transition.

clean metal and the oxide are presented. The metal spectrum is dominated by a strong $M_{23}\,M_{45}\,M_{45}$ SCK Auger emission at $\epsilon'=25$ eV. Using the UPS derived binding energies ($E_{3p}=33$ eV, $E_{3d}=1$ eV) and analyzer work function value ($\phi=4.6$ eV) the Coulomb interaction $U_{\rm eff}$ of the final-state valence-band holes is estimated to be less than 2 eV ($U_{\rm eff}=-\epsilon'+E_{3p}-2E_{3d}-\phi$).

There is, however, another broad feature in the clean metal spectrum between 37 and 45 eV. It has been observed previously and was tentatively assigned to an Auger transition involving a doubly ionized Ti core level.[11] We propose a different explanation. As evidenced by ELS and soft x-ray absorption spectroscopy (SXAS),[12,13] the 3p shell can be resonantly excited to a final state 47 eV above the ground state. If the excitation energy of the 3p shell is directly transferred to a 3d electron which is then ejected, the kinetic energy of the emitted electron is given by $\epsilon''=E_{\rm excit}-E_{3d}-\phi=41.4$. eV in good agreement with the energy actually observed.

Upon oxidation the 3d and 4s conduction-band photoemission intensity gradually disappears (see Fig. 2) and an oxide valence band (OVB) appears 5 eV below the conduction band. Consequently, both the SCK emission at 25 eV as well as the feature at 42 eV are heavily attenuated in the oxidized Ti surface [Fig. 1(b)]. Another peak, however, develops in the oxide AES at about 36 eV. Again there is no explanation at hand involving conventional Auger process. The ELS spectra of the oxidized surface[11] show a prominent peak at about 47 eV similar to the clean metal, indicating that the 3p excitation cross-section behavior in this energy range does not change much upon oxidation. Assuming a direct recombination process as in the clean metal, i.e., in this case transfer of the 3p excitation energy to a valence-band electron, the kinetic energy of the emitted electron for the oxide is given by

$$\epsilon''=E_{\rm excit}-E_{\rm OVB}-\phi=36.4\ \text{eV}$$

($E_{\rm OVB}=6$ eV). This again is in very good agreement with experiment.

If this explanation for the electron emission peaks in electron-excited AES at 42 eV in the metal and 36 eV in the oxide is correct, it follows immediately that a resonant enhancement of the valence-band photoemission in both metal and oxide should be observed: Off resonance there is only the direct photoemission, i.e., the photons are absorbed directly by valence electrons, which are thereby ejected. At resonance, however, there is an additional channel enhancing the valence-band emission. In this case the photons have a high probability of being absorbed by the 3p shell as well, which, according to the mechanism outlined above, can in turn give rise to valence-band emission by direct energy transfer from the 3p shell to the valence band. Hence, at resonance, both mechanisms should work together producing a maximum in the valence-band photoemission.

In Fig. 2 we show photoelectron distribution curves recorded at photon energies of 37 and 47 eV for the clean metal, the slightly oxidized surface, and the heavily oxidized surface. At $h\nu = 47$ eV, both the clean and the oxidized surface indeed show an enhancement of the $3d$ and OVB emission, respectively, in agreement with the model presented above. In the slightly oxidized surface [Fig. 2(b)] the peak ratio of $3d$ and $02p$ emission changes considerably when the photon energy passes through the resonance. This change occurs because, when such a channel is available, the intra-atomic deexcitation has a higher probability than the interatomic decay.[14] After exposure of the Ti(0001) surface to only 48 L O_2 [Fig. 2(c)] the conduction-band electrons are effectively removed. This is evidenced by comparison with UPS spectra of defect-free bulk-Ti_2O_3 surfaces[15] which show a significantly larger d-band emission than the spectra in Fig. 2(c). Due to the absence of $3d$ electrons a radiationless decay of the excited $3p$ shell is only possible by interaction with the OVB which therefore shows enhanced emission at resonance. This indicates the formation of a protective layer of TiO_2 even after fairly low O_2 exposures. ELS and ESD (electron stimulated ion desorption) results support this conclusion.[13,16] The remnant $3d$ emission in Fig. 2(c) is most likely due to the metal underneath the thin oxide layer and Ti^{3+} in surface defects. The resonant enhancement in the OVB emission is most pronounced for the high binding energy part of the band which is made up by bonding orbitals containing some $3d$ admixture (in contrast to the nonbonding orbitals in the upper part of the band).[15]

In Fig. 3 constant initial-state spectra (CIS) are shown for the $3d$ emission from metal and for the OVB emission from the oxide. A constant final-state spectrum (CFS) of the SCK Auger emission in the metal is also given for comparison. The resonances are broad and reflect the $3p$ excitation cross-section behavior.[17] In contrast, the CFS spectra (not included) at 42- and 36-eV kinetic energy of the metal and the oxide, respectively, show well-defined sharp peaks, namely, the resonantly enhanced $3d$ and OVB emission moving past the CFS window at the corresponding photon energy of 47 eV. This is an additional confirmation that the 36- and 42-eV peaks in the electron-excited AES do not arise from an Auger transition.

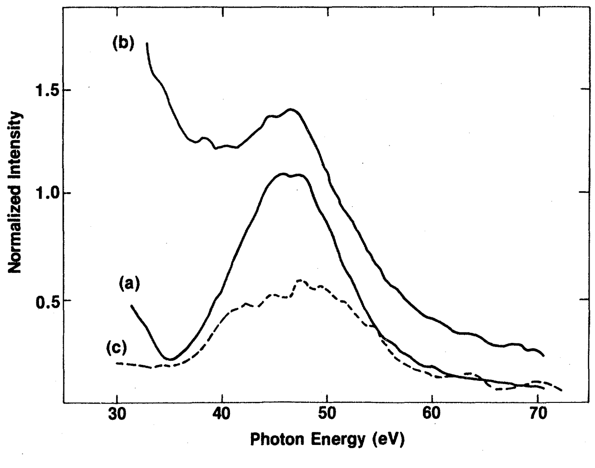

FIG. 3. CIS spectra of (a) the $3d$ photoemission in Ti(0001) and (b) the oxide valence-band photoemission in Ti(0001) +48 L O_2; (c) CFS spectrum of the $M_{23}M_{45}M_{45}$ Auger yield in Ti(0001).

We have yet to address the $3p$ excitation itself. There are two features to be noted. First, there is the delayed maximum of the cross section 14 eV above threshold. Similar delayed thresholds are well known, for example, in the case of the $4d$ excitation in the rare earths. Dehmer *et al.*[18] suggested an explanation based on the exchange interaction: The exchange integral $G'(4d,4f)$ evaluated with a collapsed $4f$ wave function is so large that it "raises" the optically favored discrete levels of a $4d^94f^{n+1}$ configuration into the "far continuum." Data obtained from atomic spectra of the transition metals[19] show that the $G'(3p,3d)$ exchange term is also large when the $3d$ orbital is collapsed. Thus, in the case of the transition metals Sc to Cr, the optically favored $3p^53d^{n+1}$ terms are raised considerably above the lowest of the $3p^53d^n$ limits and give rise to a multiplicity of strongly autoionizing levels. The theory of how these levels interact with the continuum has been developed by Starace.[20] In Ti the decay of the high-lying optically favored $3p^53d^{n+1}$ ($n=2$) levels into continua associated with the lower-lying $3p^53d^n$ terms gives rise to enhanced $3p^53d^24s^2 \rightarrow 3p^64s^2\epsilon' l$ Auger emission and the decay of those high-lying terms into the $3p^63d^{n-1}$ continua (i.e., $3p^53d^3 \rightarrow 3p^63d\epsilon'' l$) by direct recombination gives rise to the enhanced $3d$ emission. In both rare earths and transition metals the nature of the excited state depends on the detailed balance of the Coulomb potential, the centrifugal term for the $4f$ and $3d$ waves, respectively, and the exchange interaction. The effects of the exchange interaction are particularly pronounced in the transition metals, which is illustrated by ELS and SXAS data.[12] In the lower transition metals with less than half-filled $3d$ shell the $3p$ excitation onset is delayed by 10–15 eV. As soon as the half-filled shell configuration is reached in Mn, however, the clear separation of the multiplets in low-lying terms with low oscillator strength and optically favored higher terms breaks down. Therefore, in the heavier metals Mn to Ni, the maximum of the $3p$ excitation cross section occurs within a few eV above the threshold.

Another surprising feature of the $3p$ excitation in Ti is the fact that a complete transfer of the $3p$ excitation energy to the $3d$ electrons is possible. In a single electron picture this would indicate a high degree of localization of the electron in the excited state 14 eV above the Fermi level. In a local density approximation[21] the $3p$ resonance would be described as a dipole oscillation of the $3p$ shell which accounts for the localized character of the excitation in a more natural way. The atomic nature of the excitation is confirmed by the similar energy in metal and oxide.

In summary, the $3p$ excitation in Ti shows a delayed onset with cross-section maximum 14 eV above threshold. The delay is largely due to the exchange interaction in the p^5d^{n+1} configuration. For the resonantly excited $3p$ shell there are two decay channels. One is the delocalization of the excitation with subsequent Auger decay. The other is a direct recombination process where the excitation energy is transferred directly to a $3d$ or OVB electron which is subsequently emitted. This process is seen in both resonant photoemission and in the electron-excited Auger spectrum.

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