Surface Electronic Structure and Off-Site Auger Transitions on TaC(111) Observed with Auger-Photoelectron Coincidence Spectroscopy

R. A. Bartynski and S. Yang
Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849

S. L. Hulbert and C.-C. Kao
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

M. Weinert
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

D. M. Zehner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6057

(Received 19 August 1991)

The Ta N_7VV Auger spectrum of TaC(111) has been measured in coincidence with photoemission from the bulk and surface shifted Ta $4f_{7/2}$ core levels. Good agreement is found between the surface Auger spectrum and a self-convolution of the density of states (SCDOS) at surface Ta sites determined by a first-principles calculation. The bulk spectrum disagrees with the bulk SCDOS but is well described by an incoherent sum of the bulk SCDOS and the surface spectrum. A novel off-site Auger decay mechanism, first observed on Ta(100), accounts for these observations.

PACS numbers: 82.80.Pv, 73.20.−r, 79.20.Fv

Core-level binding energy shifts have been widely used to characterize the properties of solid surfaces [1]. Physical attributes ranging from chemical state and geometric structure to electronic relaxation energies and screening effects have been inferred from the magnitude and sign of surface core-level shifts (SCS) [1]. In particular, the understanding of the refractory metals Hf, Ta, W, and their carbides, which exhibit well-defined SCS of their narrow $4f$ levels on low index surfaces, has benefited greatly from this technique [2]. However, most surface properties are governed by the local valence band configuration. The ability to study the valence levels of a solid's first atomic layer would greatly enhance the fundamental understanding of these properties. Unfortunately a means of directly probing the local electronic structure of a surface atom has been lacking. Analyzing the line shape of x-ray emission [3] or core-valence-valence (CVV) Auger spectra [4] is a promising technique since the spectra are determined by the local electronic structure at the site of the core hole. However, SCS are too small for the spectrum from each site to be resolved by conventional techniques [5].

In this Letter, we describe a means of overcoming these limitations using Auger-photoelectron coincidence spectroscopy (APECS) [6,7]. By demanding coincidence between emission from the Ta N_7VV Auger transition and the surface shifted Ta $4f_{7/2}$ core level of TaC(111), we have isolated the contribution to the Auger spectrum originating from the first atomic layer and found that it is significantly different from the bulk spectrum. The line shape of the coincidence Auger spectrum was well described by a self-convolution of the valence band density of states (SCDOS) from the surface layer of a TaC(111) slab calculation [8,9]. These results indicate correlation effects are small for this surface and that APECS may be used to monitor atoms at solid surfaces as they are modified by either chemical or physical means. The Auger spectrum obtained in coincidence with the bulk (i.e., second and deeper layers) Ta $4f_{7/2}$ core level shows evidence of a novel off-site Auger transition whereby a core hole in the second Ta layer first hops to a surface Ta site before decaying. This observation and similar results obtained earlier for Ta(100) [10] indicate that such hole hopping is a general phenomenon and that off-site Auger transitions cannot *a priori* be dismissed as negligible for covalently bonded systems.

The APECS experiments were performed in an ultrahigh vacuum chamber described in detail elsewhere [7]. Briefly, two electron energy analyzers [11] are focused on a sample which was illuminated with synchrotron radiation dispersed by the U14 plane grating monochromator [12] of the VUV ring at the National Synchrotron Light Source. Coincidence Auger spectra were acquired by scanning one analyzer (the Auger analyzer) through the kinetic energy region corresponding to the Ta $N_{6,7}VV$ Auger electron spectrum of TaC(111) while the second analyzer (the photoemission analyzer) remained fixed at a kinetic energy corresponding to either the bulk or surface shifted Ta $4f_{7/2}$ core level. All kinetic energies are referenced to the Fermi level. The overall experimental resolution (electron plus photon) in each spectrum was 0.4 eV. We estimate that the cross talk between bulk and surface shifted core-level components in the photoemission channel was less than 5% [13]. When electrons were detected in both analyzers within 20 ns of each other, a coincidence event was recorded. These spectra include signals from both correlated (true) and uncorrelated (accidental) coincidence events. The accidental count rate was determined from a delayed coincidence spectrum [7]. At the same time we acquired a conventional, noncoincidence (singles) spectrum of the Auger energy re-

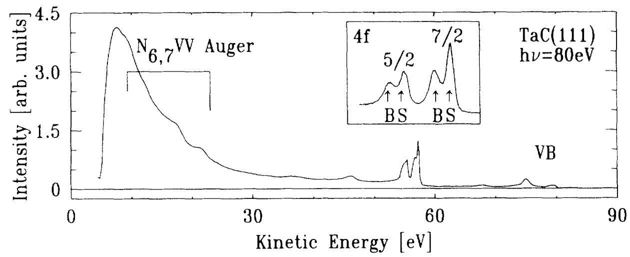

FIG. 1. Wide-scan photoemission spectrum from TaC(111) excited by 80-eV radiation. The Ta $4f_{7/2}$ and $4f_{5/2}$ core levels are expanded in the inset. Bulk and surface components are identified as B and S, respectively. The Ta $N_{6,7}VV$ $(4f5d5d)$ Auger spectral region is indicated by the bracket.

gion. The TaC(111) sample has been used in a number of previous studies [14–16]. A single 10-min sputter followed by repeated flashes to 2000°C produced a clean, well-ordered, stoichiometric surface region. We restricted the duration of our data acquisition between cleaning cycles to 20 min to ensure minimal surface contamination. The final coincidence spectrum represents the sum of approximately 100 individual spectra, each verified as free from statistical anomalies before addition.

TaC(111) was chosen for this study since it exhibits a well-resolved surface shifted Ta $4f$ core level originating from its terminal Ta layer [15,16] and the reduced carbon coordination at the surface is expected to strongly affect the valence levels of the outer Ta atoms. Figure 1 shows a wide-energy-scan photoemission spectrum from the TaC(111) surface excited by 80-eV photons. In the kinetic energy range between 55 and 60 eV, enlarged in the inset, the Ta $4f_{7/2}$ (56.65 eV) and $4f_{5/2}$ (54.7 eV) spin-orbit-split doublet is seen. Accompanying each line is a surface component shifted 0.6 eV towards E_F. The two broad features centered near 21- and 17-eV kinetic energy are identified as the Ta $N_{6,7}VV$ Auger electron spectrum.

In Figs. 2(a) and 2(b) we present Ta N_7VV Auger spectra obtained in coincidence with the surface and bulk Ta $4f_{7/2}$ core levels, respectively. Comparing the two coincidence spectra, we immediately observe that their line shapes are significantly different. Since the line shape of a CVV Auger transition is related to the valence band density of states at the site of the core hole, we conclude that *the local electronic structure of the first atomic layer of TaC(111) is significantly different from that of the bulk.*

Since the Ta valence band is dominated by a single angular momentum component ($5d$), and the bandwidth is large (7 eV) so that electron correlations should be small, the CVV Auger line shape may be approximated by the SCDOS at the Ta sites [5,10,17]. To extract the primary contributions to the coincidence spectra of Fig. 2 an approximate [18,19] inelastic secondary electron contribution (solid curve) was subtracted from the raw coincidence data yielding the primary Auger spectra presented in Fig. 3. These spectra are compared to the electronic structure of a thirteen-layer Ta terminated TaC(111) slab calculated [8] within the full-potential linear augmented-plane-wave framework [9]. From the DOS at the Ta sites for each layer, the SCDOS were computed. The solid curve in Fig. 3(a) is the SCDOS of the $5d$ levels for the first-layer Ta atoms. We find excellent agreement between the theoretical calculation and the experimental data. The 21.5- and 17-eV experimental peaks are well reproduced in energy, relative intensity, and width. Even the weak features at 13- and 11-eV kinetic energy appear

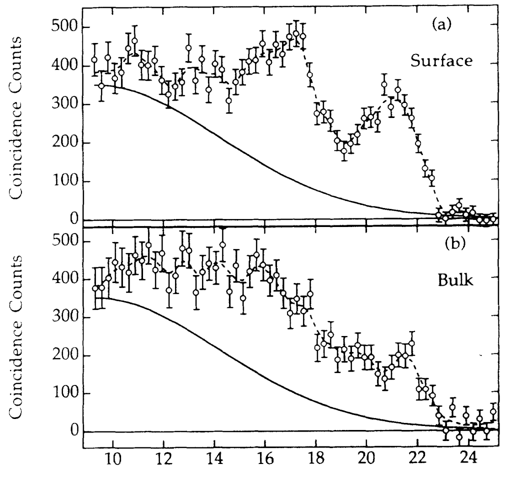

FIG. 2. Ta N_7VV Auger spectra obtained in coincidence with the (a) surface and (b) bulk Ta $4f_{7/2}$ core levels. The dashed curves represent digital smoothing of the coincidence data. The solid lines represent approximate secondary electron contributions to each spectrum (see text).

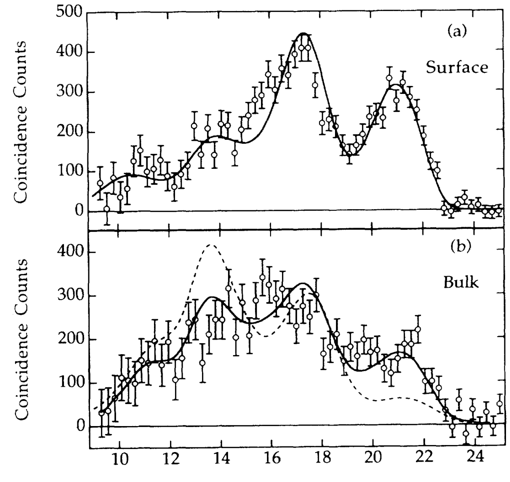

FIG. 3. Primary (a) surface and (b) bulk N_7VV Auger spectra obtained by subtracting the solid curve from the data in Fig. 2. The solid curve in (a) is the SCDOS from the first Ta layer. The dashed curve in (b) is a weighted sum of the SCDOS from second and deeper layers. The solid curve in (b) is the average of the experimental surface Auger spectrum and the SCDOS from second and deeper layers.

in both curves. The only disagreement occurs near 16 eV where a shoulder seen in the data is absent in the calculation. This small feature may be due to matrix element effects not considered here. The excellent agreement obtained here implies that APECS can be used to probe the electronic structure of a single atomic layer in a solid [20] and supports the assertion [15,16] that the TaC(111) surface is Ta terminated.

In Fig. 3(b) we compare the SCDOS from the second layer and deeper Ta sites (dashed curve) to the APECS spectrum taken in coincidence with the bulk Ta $4f_{7/2}$ core level. Here there is rather poor agreement between the experimental spectrum and the theoretical prediction near 21, 16, and 13.5 eV. It is unlikely that these discrepancies are the result of deficiencies in our electronic structure calculations [8] as they are consistent with several previous theoretical studies [21,22] of bulk TaC and have successfully predicted the surface Auger spectrum. The most probable explanation is the presence of an additional, significant decay channel for a subsurface core hole which has not yet been considered.

A likely candidate for this decay mode is suggested by the differences between the data and the dashed curve. Note that the additional spectral weight above 19 eV occurs where strong emission is seen in the surface Auger spectrum. This observation can be explained if core holes created in subsurface Ta atoms can undergo Auger decay via emission of valence electrons from surface Ta atoms. Figure 4 schematically illustrates two ways that this may occur. Panel (b) is an off-site Auger decay. Here a subsurface valence electron fills the Ta core hole, ejecting a valence electron from a surface Ta site. Assuming similar electron densities at surface and bulk sites, the ratio of the transition rate for this process to that of an on-site Auger process, Γ_A^n/Γ_A^o, is given by the ratio of off-site to on-site Auger matrix elements: M_A^n/M_A^o [10,23]. Similar to the elemental Ta case [10], we estimate this ratio to be approximately 10^{-2} indicating that this process does not occur at a rate which is sufficient to account for the extra emission we observe. A lower electron density and smaller matrix elements [8] make off-site transitions involving the C atoms even less likely.

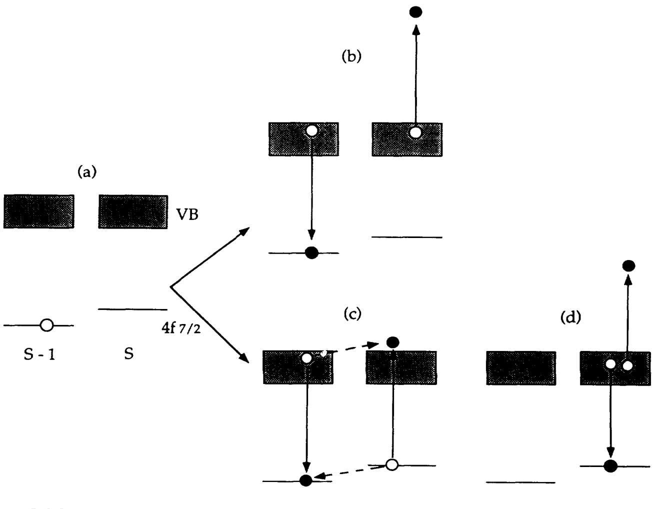

FIG. 4. Possible decay modes of a subsurface core hole which involve surface valence electrons. The shaded rectangles represent the valence band and the horizontal lines the Ta $4f_{7/2}$ core levels. S denotes surface; S − 1 denotes subsurface. (a) The Auger initial state with a core hole in the subsurface site. (b) Conventional interatomic Auger decay. (c) Hole hopping leading to (d) surface on-site Auger decay.

An alternative, energetically allowed off-site Auger process, originally proposed [10] to explain coincidence data from Ta(100), is schematically represented in Figs. 4(c) and 4(d). Here the core hole in the subsurface Ta $4f_{7/2}$ level hops to the surface core level (exciting an electron-hole pair) [panel (c)] and then decays by a surface on-site Auger decay [panel (d)]. There are two paths by which this core hole can hop. Direct hopping, given by the dashed arrows in panel (c), involves the overlap of $4f$ wave functions on neighboring sites and hence occurs at a negligible rate [10]. In the second route, indicated by the solid arrows in panel (c), the subsurface core hole is filled by a subsurface valence electron, and the excess energy is dissipated by the excitation of the neighboring surface $4f_{7/2}$ core electron to an unoccupied state just above the Fermi level. The transition rate for this process is given by [10]

$$\Gamma_H^o \propto M_H N_c \int de\, g_o(e) g_n(e + (e_c^n - e_c^o)) \,,$$

where M_H is the hopping matrix element [23], N_c is the degeneracy of the $4f_{7/2}$ core level, g_o (g_n) is the occupied (unoccupied) density of states at the core hole (neighboring) site, and e_c^o (e_c^n) is the binding energy of the respective core holes.

The rate of this process, Γ_H^o, is much greater than Γ_A^n for several reasons: The matrix element [23] involves the overlap of $4f$ and $5d$ wave functions *at the same site;* the joint density-of-states factor is large for TaC(111); and the large degeneracy of the core level ($N_c = 8$) enhances this process by almost a factor of 10. We estimate the rate for this process to be the same order of magnitude as the on-site Auger decay rate. As a result, there will be a contribution to the subsurface Auger spectrum which has the shape of the surface Auger spectrum. The solid curve in Fig. 3(b) is an incoherent sum of the experimental surface spectrum and the subsurface Ta $5d$ SCDOS, each given equal weight. Clearly, this curve shows significantly better agreement with the data than does the bulk curve alone. The threshold region is well reproduced and the 13.5-eV feature is now consistent with the data. The small discrepancy near 16 eV is most likely the bulk analog of the slight disagreement found for the surface spectrum. From this semiquantitative account of the bulk spectrum, we conclude that the *probabilities of off-site and on-site Auger decay can be of the same order of magnitude for covalent systems.*

The existence of off-site transitions will impact conventional Auger spectroscopy in several ways. With hole hopping, the singles Auger spectrum will be more (less) surface sensitive than an exponentially decreasing sum of contributions from successively deeper layers if the subsurface (surface) core level is more tightly bound than the surface (subsurface) core [cf. Ta(100)] [10]. The off-site Auger transition also provides an additional decay channel for the deeper core hole that manifests itself as a greater lifetime broadening of this core level as observed for Ta(100) [10]. In a recent study of alkali metal overlayers on Be, there was evidence in the line shape of the overlayer *CVV* Auger spectrum suggesting the participation of substrate electrons [24]. More generally, off-site Auger processes may play an important role in other physical phenomena. Recently, there has been an increased interest in the participation of hot carriers [25,26] in the stimulated desorption process. Since the core hole hopping mechanism excites electron hole pairs, it may have a significant influence on desorption yields associated with core photoexcitation [27].

The authors would like to thank Professor E. Jensen for stimulating discussions. Support from the Rutgers University Research Council and the National Synchrotron Light Source staff is gratefully acknowledged. The National Synchrotron Light Source is funded by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016. One of us (D.M.Z.) was supported by Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

---

[1] W. F. Egelhoff, Surf. Sci. Rep. **6**, 253 (1987), and references therein.

[2] D. Spanjaard, C. Guillot, M. C. Dejonqueres, G. Treglia, and J. Lecante, Surf. Sci. Rep. **5**, 1 (1985), and references therein.

[3] *Soft X-Ray Band Structure and the Electronic Structure of Metals and Materials,* University of Strathclyde, Scotland Conference Proceedings, edited by D. J. Fabian (Academic, London, 1968), and references therein.

[4] G. D. Davis and M. G. Lagally, J. Vac. Sci. Technol. **15**, 1311 (1978).

[5] J. E. Houston and R. R. Rye, in *Auger Electron Spectroscopy,* edited by C. L. Briant and R. P. Messmer (Academic, San Diego, 1988), p. 65.

[6] G. A. Sawatzky, in Ref. [5], p. 168.

[7] E. Jensen, R. A. Bartynski, S. L. Hulbert, and E. D. Johnson, Rev. Sci. Instrum. (to be published).

[8] The calculation was performed for the minimum energy surface which has a 12% inward relaxation; M. Weinert (unpublished).

[9] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571 (1982).

[10] E. Jensen, R. A. Bartynski, M. Weinert, S. L. Hulbert, E. D. Johnson, and R. F. Garrett, Phys. Rev. B **41**, 12468 (1990).

[11] Physical Electronics, Eden Prairie, MN, model 15-225G.

[12] G. P. Williams, M. R. Howells, N. Lucas, and P. Z. Takacs, Nucl. Instrum. Methods **222**, 99 (1984).

[13] The contribution from the surface core level to the signal acquired while the photoemission analyzer is fixed at the kinetic energy of the bulk core level is estimated by the overlap of a Gaussian of energy width equal to the photon energy resolution (0.3 eV) centered at the surface core level with a Gaussian of energy width equal to the electron energy resolution (0.25 eV) of the cylindrical mirror analyzer centered at the kinetic energy of the bulk core level.

[14] G. R. Gruzalski and D. M. Zehner, Phys. Rev. B **42**, 2768 (1990).

[15] S.-C. Lui, D. M. Zehner, G. R. Gruzalski, and D. Heskett (unpublished).

[16] A recent LEED *IV* study [H. L. Davis, B. Dötsch, and D. M. Zehner, J. Vac. Sci. Technol. (to be published)] indicates that the surface is Ta terminated.

[17] D. R. Jennison, Phys. Rev. Lett. **40**, 807 (1978).

[18] For other systems (cf. Ref. [19]), we have observed a significant contribution to coincidence Auger spectra from intrinsic secondaries; however, this emission exhibits no structure. In addition, from the lack of features in the loss spectrum of the TaC core levels (only Ta $5p$'s are seen below the $4f$ levels in Fig. 1) we approximate the secondary electron background with a smooth monotonic function. The conclusions we reach do not depend on the detailed nature of this shape.

[19] E. Jensen, R. A. Bartynski, R. F. Garrett, S. L. Hulbert, E. D. Johnson, and C.-C. Kao (to be published).

[20] S. L. Hulbert, C.-C. Kao, R. F. Garrett, R. A. Bartynski, S. Yang, M. Weinert, E. Jensen, and D. M. Zehner, J. Vac. Sci. Technol. A **9**, 1991 (1991).

[21] B. M. Klein, D. A. Papaconstantopoulos, and L. L. Boyer, Phys. Rev. B **22**, 1946 (1980).

[22] G. H. Schadler, A. M. Boring, P. Weinberger, and A. Gonis, Phys. Rev. B **38**, 9538 (1988).

[23] A detailed discussion of the matrix elements relevant to these transitions is given in Ref. [10].

[24] P. A. Bruhwiler and E. W. Plummer (unpublished).

[25] S. A. Buntin, L. J. Richter, D. S. King, and R. R. Cavanagh, J. Chem. Phys. **91**, 6429 (1989).

[26] X.-L. Zhou, X.-Y. Zhu, and J. M. White, Surf. Sci. Rep. (to be published).

[27] T. E. Madey, D. L. Doering, E. Bertel, and R. Stockbauer, Ultramicroscopy **11**, 187 (1983).

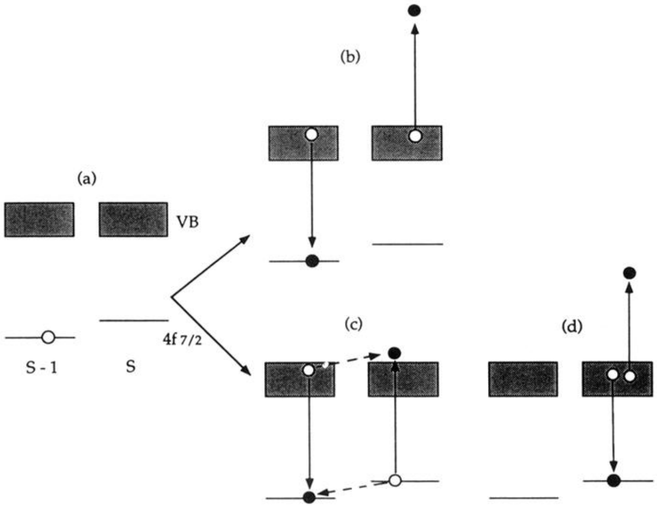

FIG. 4. Possible decay modes of a subsurface core hole which involve surface valence electrons. The shaded rectangles represent the valence band and the horizontal lines the Ta $4f_{7/2}$ core levels. S denotes surface; $S-1$ denotes subsurface. (a) The Auger initial state with a core hole in the subsurface site. (b) Conventional interatomic Auger decay. (c) Hole hopping leading to (d) surface on-site Auger decay.