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Unoccupied electronic resonances of Sc adsorbed on W(001) by *k*-resolved inverse photoemission

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Scandium adsorbed on the (001) face of tungsten has been studied using Auger-electron spectroscopy, low-energy electron diffraction, *k*-resolved inverse photoelectron spectroscopy, work-function measurements, and relativistic-electronic-structure calculations. We find that the work function of W(001) does not decrease monotonically as a function of scandium adsorption but reaches a minimum value of $\phi=3.25$ eV at 50% coverage. For a complete monolayer, an order 1×1 Sc overlayer is formed. Inverse photoemission in the isochromat mode was used to map the unoccupied energy levels of this overlayer along the $\overline{\Gamma}\,\overline{M}$ symmetry direction of the surface Brillouin zone. Local-density-functional calculations using the muffin-tin orbital method were performed for a 1×1 Sc overlayer on W and are compared with the experimental two-dimensional band structure.

I. INTRODUCTION

Many investigations of chemisorption have involved alkali-metal and alkaline-earth elements as the adsorbates.[1] These materials have widespread use as electron emitters and constitute some of the key elements in the fabrication of electron devices. Transition-metal adsorption on metal surfaces has been studied in considerably less detail. Nevertheless, there has been considerable recent interest in Sc adsorption on metals such as W.[2] In large part, this is due to the cathode design involving this material which was recently proposed by van Oostrom and Augustus.[3]

Most experimental studies of Sc adsorption on W have been performed with the aim of obtaining information on the atomic arrangement of the adsorbate and on the reduction of the work function produced by chemisorption.[4–7] However, a study of the electronic structure of these materials is important for understanding the role played by the localized *d* states of the substrate and the valence electrons of the adsorbate in the interaction.

The occupied energy levels of the adsorbate are commonly studied using photoelectron spectroscopy. The unoccupied electronic *d* states over few electron volts above the Fermi level are also known to be equally important in chemisorption systems. With the use of the *k*-resolved inverse photoelectron spectroscopy (IPS) technique, information about the empty *d* states of transition metals and their role in the adsorption on other metals can be obtained. It is of course most useful if such data could be compared with theoretical band-structure calculations.[8]

In this study, we present Auger-electron spectroscopy (AES), low-energy electron diffraction (LEED), IPS, and work-function ($\Delta\phi$) data for the (001) surface of W overlaid with Sc. The IPS measurements are compared with the results of first-principles electronic structure calculations for a 17-layer slab of W atoms covered with 1 ML of Sc.

II. EXPERIMENTAL TECHNIQUES

The experimental setup has been described in detail elsewhere.[9,10] IPS measurements were performed in the isochromat mode at a photon energy of 9.8 eV. The divergence of the electron beam is estimated to be $\Delta\theta=3°$ which results in a momentum resolution of $\Delta k_{\parallel}=0.1$ Å^{-1}. The overall energy resolution of the spectrometer is approximately 0.6 eV.[11]

Scandium was evaporated onto the W(001) surface from a resistively heated source at pressures in the low 10^{-10}-Torr range. The target was held at room temperature during evaporation. To produce the ordered overlayers, films several layers thick were initially deposited. The crystal was then annealed at appropriate temperatures.[5] The surface concentration was determined by a combination of evaporation times, $\Delta\phi$, LEED, and AES measurements. We used the ratio of the Sc *LMM* to the W *MNN* Auger peak intensities, rather than the intensities of Sc and W individually, to eliminate any deviations due to variations in the electron-beam intensity between runs. The method of "break points" was used to determine the point of monolayer coverage.[12] The change in the work function of the W(001) surface was monitored continuously during evaporation using the retarding field method as described in a previous publication.[10]

III. COMPUTATIONAL METHOD

In order to interpret the IPS measurements, first-principles self-consistent supercell electronic structure calculations were carried out for a 1×1 Sc monolayer on W(001). The calculations were carried out in the framework of the density-functional theory[13] in the local-density approximation (LDA) with the Hedin-Lundqvist parametrization of the exchange and correlation.[14] The scalar relativistic linear muffin-tin orbital (LMTO) method[15] was used in the atomic-sphere approximation

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(ASA). The surface band-structure calculations were performed for slabs of W of various thicknesses with a monolayer of Sc atoms placed on each side of the slab. It was found that convergent results were achieved for slabs consisting of 17 layers of W atoms. We believe that these are the largest slabs studied self-consistently. All interlayer distances, including the W-Sc separation, were taken to be 1.58 Å, corresponding to the interlayer spacing of the bulk W crystal in equilibrium. Seven layers of empty spheres were used to simulate the vacuum. The integrations were performed with the tetrahedron method in a regular mesh of 625 points in the surface Brillouin zone (SBZ) of the two-dimensional square lattice. With the exception of a systematic overestimate of the work function by the ASA method, we find that this model provides an accurate description of the electronic wave functions in the surface and vacuum regions as well as in the bulk. In order to reveal the changes in the surface band structure of W(001) due to the Sc overlayer, calculations corresponding to the pure unreconstructed W(001) surface were also carried out. The two-dimensional band structure obtained for a 19-layer supercell of the unreconstructed surface is found to be in excellent agreement with the results of earlier linear augmented-plane-wave calculations.[16]

IV. RESULTS AND DISCUSSION

A. Work-function measurements and thin-film morphology

Figure 1(a) shows the variation of the Sc *LMM* and the W *MNN* Auger peak-to-peak heights as a function of Sc evaporation time. This plot shows well-defined linear portions of the Sc and W Auger peak intensity versus evaporation time curves which end at approximately 6 min. The breaks correspond to the formation of 1 ML. Furthermore, no break points are observed at higher coverage. This is typical behavior for Stranski-Krastanov-type growth where crystallite formation occurs after deposition of 1 ML.[12]

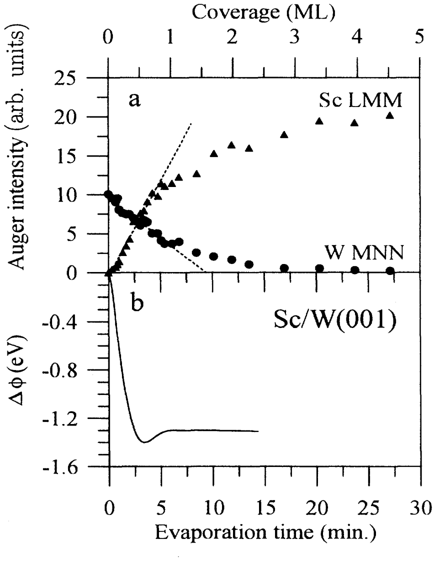

FIG. 1. (a) Sc *LMM* and W *MNN* Auger peak intensities and (b) variation of the work function of the W(001) surface as a function of scandium adsorption.

The variation of the work function of the W(001) crystal versus Sc evaporation time is presented in Fig. 1(b). The results of point-by-point measurements at room temperature by Voronin,[4] and Gorodetskii and Yas'ko[5] indicated that the work function of the W(001) surface decreased continuously as a function of scandium adsorption reaching a saturation value of $\phi \approx 3.3$ eV at a coverage of 1 ML. By monitoring $\Delta\phi$ continuously, we find that the work function does not decrease continuously from that of W(001) ($\phi = 4.63$ eV) (Ref. 17) to that of bulk Sc ($\phi = 3.5$ eV) (Ref. 18) as a function of coverage. Instead, it reaches a minimum value of 3.25 eV for an evaporation time of approximately 3 min then rises again and reaches a saturation value of 3.36 eV for an evaporation time of 6 min corresponding to the formation of a complete monolayer. The ratio of Sc *LMM* to the W *MNN* Auger peak intensities is approximately 1.3 at 50% coverage and 3.1 at full coverage. Our value of the work function of the Sc/W(001) system at saturation is in good agreement with the saturation values reported by Voronin,[4] and Gorodetskii and Yas'ko[5] despite the disagreement at lower coverage. It is possible that contamination of the W(001) crystal and/or the scandium source due to the rather poorer vacuum conditions (10^{-9} Torr or worse) may have resulted in a structureless $\Delta\phi$ versus Sc coverage in their room-temperature measurements. In fact a minimum in the work function of W(001) versus Sc coverage was observed at half a monolayer by Kultashev and co-workers[6,7] but only at elevated temperatures, i.e., 1100 K.

With the target held at room temperature, no new LEED diffraction patterns are observed during evaporation. After completion of 1 ML, the intensity of the LEED spots of the 1×1 structure decreases gradually and vanishes when the coverage reaches 4 ML. When Sc films more than three layers thick are annealed at 1300 K, a sharp 1×1 LEED pattern reappears. The corresponding Auger peak-intensity ratio is approximately 2.9 and is similar to that of the unannealed monolayer films. In addition to giving a similar Auger peak-intensity ratio (~ 3), the annealed and unannealed films corresponding to 1 ML of Sc on W(001) give similar IPS spectra and LEED structures. However, the annealed samples produce much sharper spots. The dependence of the intensity of these spots on energy appears to be different from that of pure W(001). Gorodetskii and Yas'ko[5] attribute this LEED pattern to the formation of fcc Sc crystals, the (001) face of which is parallel to that of the backing W(001) surface.

When thick Sc overlayers are annealed at 1700 K, a $c(2\times2)$ LEED pattern appears. The same LEED pattern is observed when Sc films one layer thick or less are heated to only 1200 K. Auger analysis yields a Sc *LMM* to W *MNN* peak-intensity ratio of approximately 0.6 for these films. This ratio is much lower than that corresponding to half monolayer films, 1.3, obtained from the room-temperature Sc deposition using the extent of the linear regions of the Auger peak-intensity curves and the minimum value of the work function. We believe that annealing at high temperatures (~1700 K) results in large areas of the W(001) substrate being exposed giving large residual substrate signals and hence a smaller ratio. This suggests that the thick Sc films deposited at room temperature transform to thermodynamically stable islands when annealed at 1700 K. Observation of such kinetic effects at lower temperatures for thin overlayers tends to support this argument. Such a transformation to stable island structures is similar to that observed for silver deposited on nickel.[19] We believe that it is these islands that give rise to the $c(2\times2)$ LEED structures since sharp well-defined LEED patterns can arise from surfaces covered with only a fraction of a low-index plane.[20]

B. IPS measurements and calculated local density of states (LDOS)

Figure 2 shows a series of IPS spectra from W(001) taken at normal electron incidence ($k_{\parallel}=0$) as a function of Sc coverage (Θ_{Sc}). The measurements are normalized to the incident-beam current and the Fermi edge is determined from the onset of photon emission. The clean W(001) spectrum exhibits a broad peak centered around E_F+3 eV. Near normal incidence, this peak has been shown to result from transitions to W bulk and surface states.[21] At a coverage of only $\frac{1}{4}$ ML, this peak is noticeably attenuated and a new feature appears near $E_F+0.6$ eV. The intensity of this peak increases with Sc adsorption and reaches a maximum at $\Theta_{\mathrm{Sc}}\approx1$ ML. Further increase in coverage results in a gradual attenuation of its intensity. In addition, there appears to be a slight movement of this peak with increasing adsorption. As the coverage increases, this peak first moves towards the Fermi level, reaches a minimum energy of 0.2 eV at $\Theta_{\mathrm{Sc}}=1$ ML, then shifts away from the Fermi level and remains stationary near 0.5 eV at higher coverage. Although these energy shifts are comparable to the resolution of our spectrometer they are reproducible. We assign this peak to transitions to empty Sc 3*d* states since they are the lowest unoccupied levels. Bremsstrahlung isochromat spectroscopy measurements for bulk Sc by Speier *et al.*[22] do not show unoccupied states near the Fermi level presumably due to the rather poorer resolution of their spectrometer. In fact, their calculations show an unoccupied Sc state at the Fermi level which is smeared out when instrumental and lifetime broadenings are taken into account.

For a coverage of $\Theta_{\mathrm{Sc}}\approx\frac{3}{4}$ ML, a weak peak appears near E_F+4 eV, i.e., 0.64 eV above the vacuum level. The intensity of this peak increases with coverage and reaches a maximum value at 1 ML. It disappears when the coverage reaches 1.5 ML presumably due to its merging with the W(001) bulk state near 3 eV. A similar state was observed by Hu *et al.*[23] for scandium adsorption on highly oriented pyrolytic graphite.

IPS spectra for a coverage of 1 ML are presented in Fig. 3 for varying angles of electron incidence (θ) with the direction of $k_{\parallel}$ fixed along the $\bar{\Gamma}\bar{M}$ symmetry line of the SBZ. The lower Sc unoccupied state is seen to disperse from 0.2 eV at normal incidence to 1.8 eV at $\theta=45°$. The higher unoccupied state appears at about 4 eV above the Fermi level and also shows upward dispersion with increasing θ. It disappears at 4.9 eV for

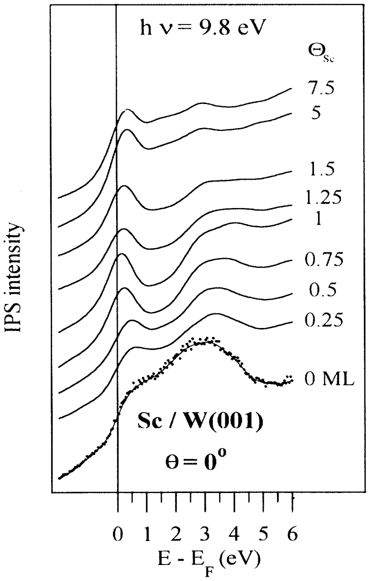

FIG. 2. Sequence of inverse photoemission spectra of scandium on W(001) as a function of scandium coverage (Θ_{Sc}). The spectra are recorded at normal incidence, i.e., $k_{\parallel}=0$.

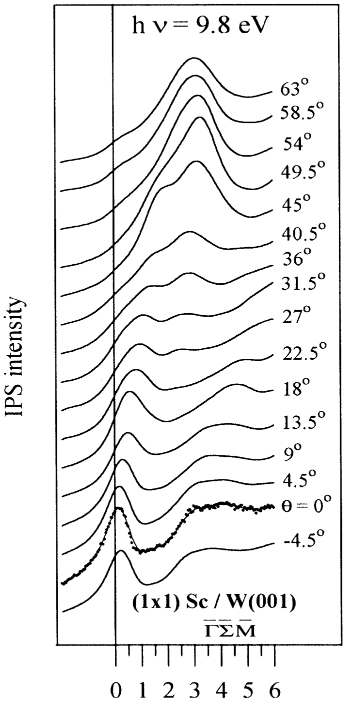

FIG. 3. Inverse photoemission spectra for 1 ML ($\Theta_{\mathrm{Sc}}=1$ ML) of scandium on W(001) for various angles of electron incidence (θ) with $k_{\parallel}$ fixed along the $\bar{\Gamma}\bar{M}$ symmetry direction of the SBZ.

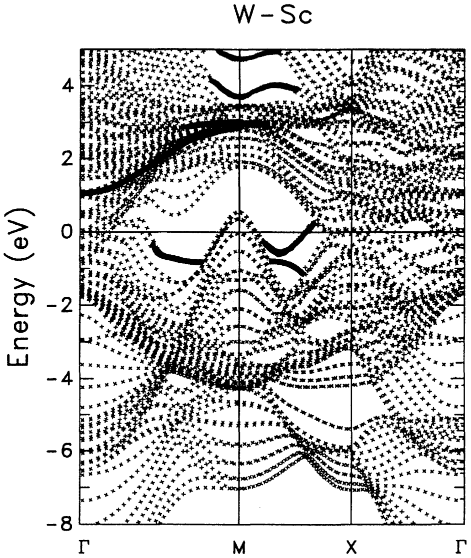

FIG. 4. Calculated two-dimensional band structure for 1 ML of Sc atoms placed on both sides of a 17-layer W slab. Crosses indicate eigenvalues of the slab and the thick lines represent surface states and resonances. The density of symbols provides a visual impression of the density of states. The main pockets in the projected band structure can easily be identified although their borders are only given approximately by the eigenvalues of the slab because of size quantization.

$\theta=22.5°$. The state which appears at $E_F+2.6$ eV near $\theta=27°$ is assigned to transitions to bulk W states and has been discussed in detail elsewhere.[21]

Figure 4 displays the band structure of a 19-layer Sc-capped slab. The surface states and resonances are indicated by dark solid lines. The k-resolved LDOS of the top Sc layer and of bulk W are represented in Fig. 5 by solid and dashed lines, respectively, for eleven points along the $\overline{\Gamma}\,\overline{M}$ axis. The experimental two-dimensional band structure for 1 ML of Sc on W(001) as derived from the spectra of Fig. 3 is compared with the theoretically predicted k-resolved LDOS in Fig. 6. The dots indicate peak positions in the IPS spectra while the solid and dashed lines represent the contributions to the LDOS from the d states on the Sc layer and the first W layer, respectively. While a more detailed description of the theoretical approach will be published elsewhere,[24] we present here some important features of these results which are relevant to the interpretation of the IPS spectra. Analysis of the band-structure calculations and comparison with the IPS data reveal the following.

(1) In order to ensure convergence and eliminate accidental peaks in the k-resolved LDOS which occur for thin slabs, we employed large supercells containing 19 atomic and 7 vacuum layers.

(2) While the local densities of states on the Sc surface layer and the first W layer have well-pronounced surface states, the local densities of states for the second and third W layers are already similar to those of bulk states.

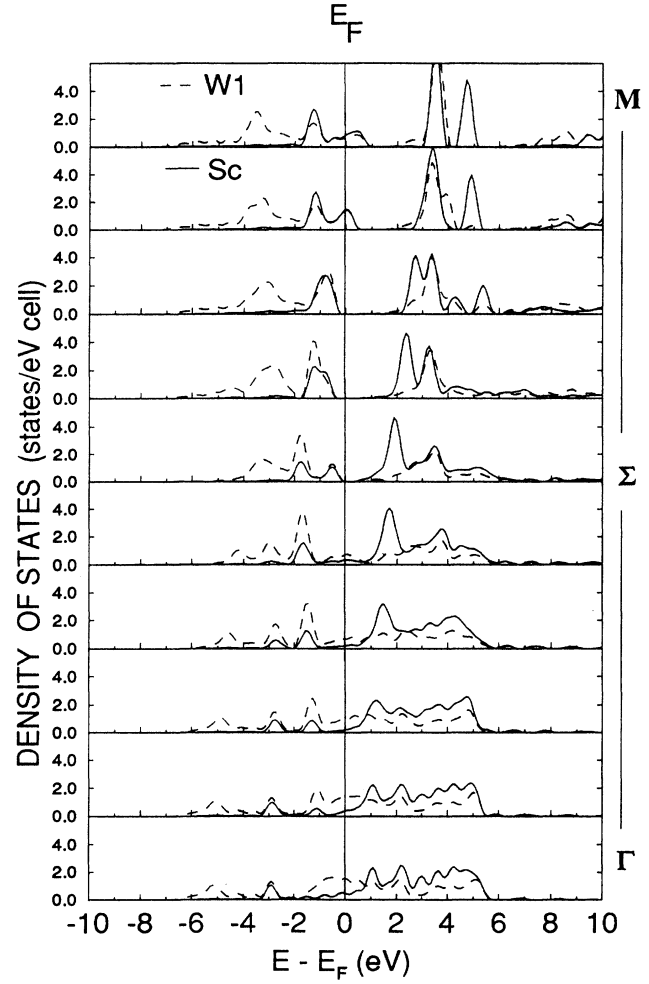

FIG. 5. Contributions of d states to the LDOS from the Sc layer (solid lines) and the first W layer (dashed lines) for 1 ML of Sc placed on both sides of a 17-layer W slab.

(3) The main feature in the calculated LDOS is a Sc-related unoccupied surface resonance state which lies slightly above the Fermi level at the $\overline{\Gamma}$ point and has a significant dispersion in the $\overline{\Gamma}\,\overline{M}$ direction (peak R, Fig. 6). Aside from lying ~ 0.5 eV higher, the calculated peak exhibits the same dispersion as found in the IPS measurements. In addition, the calculated peak disappears at $k_{\|}\approx 0.8$ Å^{-1} along the $\overline{\Gamma}\,\overline{M}$ line in good agreement with experiment. The observed systematic difference of ~ 0.5 eV between the theoretical results and the experimental measurements for this surface resonance peak may be the consequence of the ASA and/or the fact that the lattice relaxation effects were ignored. However, the good agreement between the dispersions of the calculated and measured peaks allows us to identify this peak as a Sc antibonding d state.

(4) We predict another Sc-induced unoccupied surface state which lies ~ 3.5 eV above the Fermi level near the $\overline{M}$ point (peak S, Fig. 6). However, this state is not ob-

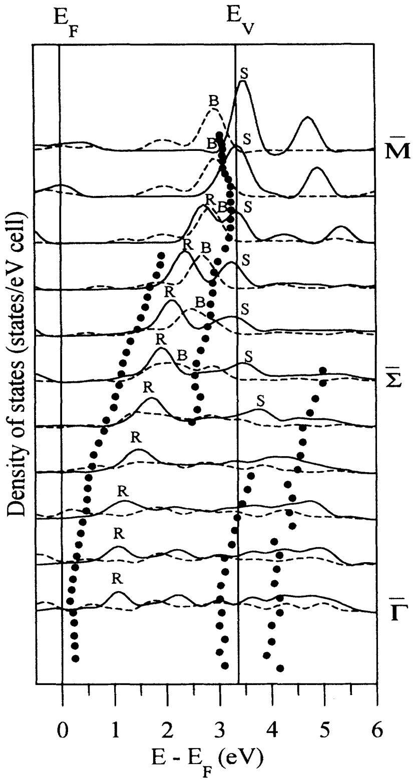

FIG. 6. Comparison of the experimental two-dimensional band structure with calculated k-resolved LDOS for a (1×1) scandium monolayer on W(001). Dots represent the experimentally determined peak positions. Solid and dashed lines correspond to the scandium and tungsten contributions to the LDOS, respectively. E_v is the measured vacuum level.

served in the IPS spectra presumably because of broadening due to its proximity to the vacuum level.

(5) We also find a relatively nondispersing W-related occupied surface state located at 1 eV below the Fermi level (see Fig. 5). This state is formed mainly by W 5d orbitals and merges with the continuum of the extended states near the middle of the $\bar{\Gamma}\bar{M}$ line. This state and the Sc-induced unoccupied resonance state located near the Fermi level can be viewed as a covalent bonding-antibonding pair of W (5d)–Sc (3d) states at the surface.

(6) In addition, we predict a W bulklike state near 3 eV above the Fermi level (peak B, Fig. 6). The $k_{\parallel}$ value at which this state appears and its dispersion along the $\bar{\Gamma}\bar{M}$ line are in good agreement with the IPS measurements.

(7) In agreement with the experimental measurements, the calculations show a substantial reduction in the work function upon Sc adsorption. The calculated work functions for the bare and Sc-covered W surfaces, 7.8 and 5.3 eV, are larger than the corresponding measured values of 4.6 and 3.3 eV. The overestimates are attributable to the ASA and possibly to the neglect of the relaxation of the surface layer.[25]

V. SUMMARY

We have studied the properties of Sc adsorbed on W(001) using AES, LEED, IPS, $\Delta\phi$ measurements, and LMTO LDA calculations. In contrast to previous studies, we find that the room-temperature adsorption of Sc on W(001) does not result in a monotonic decrease of the work function with increasing coverage. Rather, the work function decreases to a minimum value of 3.25 eV at half a monolayer coverage then rises again to a saturation value of 3.36 eV at a coverage of 1 ML. Using IPS in the isochromat mode, we observe Sc-induced unoccupied states some of which appear as sharp resonances and show coverage-dependent shifts consistent with previous IPS studies. Comparison of the experimental measurements with the theoretical calculations provides an identification of the peaks observed in IPS as Sc surface-like resonances and W bulklike states. Further theoretical calculations going beyond the approximations employed in this work are in progress.

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