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Surface barrier in W(110). I. Self-consistent film calculations

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Self-consistent electronic-structure calculations have been performed for a five-layer film of W(110), with particular reference to the form of the potential barrier. The calculated potential distribution and the surface barrier are compared with results previously obtained for the W(001) surface. Information about the surface-state distributions is provided by the projected densities of states in the different layers.

I. INTRODUCTION

The potential barrier at a metal surface has been a subject of continuing interest and importance for many years. Most probes of surface electronic structure involve the interaction of a charged particle with the surface, and there have been numerous simple models discussed.[1] On the basis of self-consistent electronic-structure calculations for a five-layer W(001) film, the following barrier form was proposed recently:[1]

$$V(z)=\begin{cases}\{1-\exp[\lambda(z-z_0)]\}/[2(z-z_0)], & z<z_0\\ -U_0/\{A\exp[-B(z-z_0)]+1\}, & z>z_0\ .\end{cases} \tag{1}$$

A and B are constants determined by matching $V(z)$ and its normal derivative at the image plane z_0, where the potential has the value $-\lambda/2$. Far from the surface the potential has the image form (relative to z_0) and it has a smooth transition to the bulk inner potential U_0. Although the potential at the W(001) surface has a pronounced three-dimensional character, a barrier of the form (1) with $z_0=-2.9$ a.u. and $\lambda=1.1$ a.u.$^{-1}$ provides a satisfactory description of the parallel average of the potential of the film calculations[1] in the transition region between bulk and vacuum.

The potential which results from the film calculations is appropriate to occupied states, and the effective potential experienced by incident electrons with energies above the vacuum level will be different. In the case of W(001), however, a barrier of the form (1) with modified parameters reproduces high-resolution low-energy electron diffraction (LEED) measurements very well in the range 0–35 eV.[1,2] Other barrier models have also been proposed. A recent suggestion of Baribeau *et al.* uses the same form as (1) outside the surface, but allows the inner potential in the surface layer to differ from the bulk value. Based on an analysis of high-resolution LEED data, these authors concluded that the inner potential in the outermost layer is nearly 4 eV less than the bulk value in W(001), but only 0.5 eV less in W(110). The location of the image plane was found to be significantly closer to the surface in the case of the more densely packed (110) surface ($z_0=-2.72$ a.u.) than in W(001) ($z_0=-3.67$ a.u.).

There have been several calculations of the electronic structure of W(001) surfaces,[4–6] and several model calculations have been performed for the W(110) surface.[7–10] However, no self-consistent, parameter-free calculations of the latter are known to us. In view of the valuable complementary roles played by electronic-structure calculations and LEED analysis in W(001), we have performed both sets of calculations for the W(110) surface. In the present work, we describe and discuss self-consistent density-functional calculations for a five-layer film, paying particular attention to the differences between the two surfaces. In a companion paper,[11] we determine the barrier of form (1) which provides the best description of available high-resolution LEED data.[3]

The method used in the calculations has been described in detail elsewhere.[12] We outline in Sec. II those features necessary in the present context, and compare the calculated potential distribution with that found previously for W(001). Section III discusses other features of the results, in particular, the densities of states in the different layers, and we summarize our findings in Sec. IV.

II. SELF-CONSISTENT FILM CALCULATIONS—W(110)

Details of the method are given in Ref. 12. The effect of surface relaxation and reconstruction is small in W(110),[7,13] and we consider here a five-layer W(110) film with a geometry unchanged from that in the bulk. The atomic positions and the corresponding surface Brillouin zone[14] (SBZ) are shown in Fig. 1. The solution of the single-particle Schrödinger-like equations with the full potential are performed using the linear-augmented-plane-wave method[12] and assume a local-density approximation for exchange and correlation.[15] All relativistic effects, except spin-orbit coupling, were included. More than 60 basis functions per atom were used, leading to mRy accuracy in the eigenvalues. Integrations over the SBZ were performed using the linear triangular method[12] with 25 points in the irreducible part ($\frac{1}{4}$) of the SBZ (see Fig. 1).

The local-density approximation for the exchange-

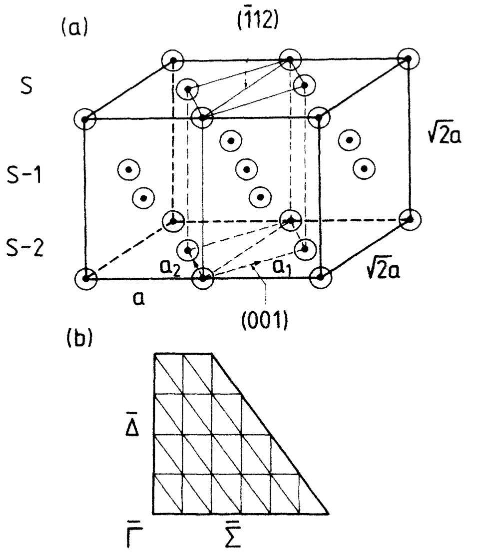

FIG. 1. (a) Geometry of (110) surface of a bcc crystal, showing surface (S), subsurface ($S-1$), and central ($S-2$) layers. (b) Corresponding irreducible part of the surface Brillouin zone. The 25 points used in the k-space integrations are indicated.

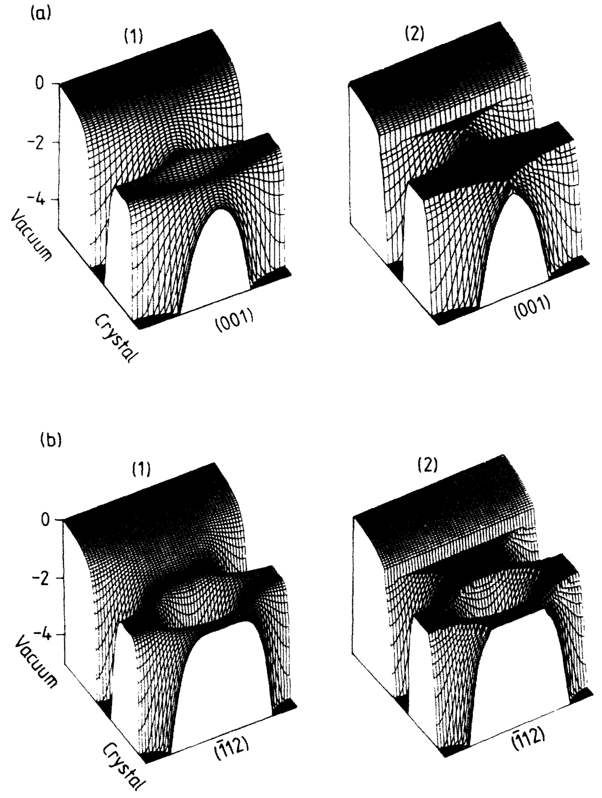

FIG. 2. Variation of self-consistent potential for W(110) film in two planes perpendicular to the surface (see Fig. 1). Part (1) is the total potential and part (2) the muffin-tin component (in rydberg units).

correlation potential leads to some well-known inaccuracies, with energy differences requiring particular caution. In spite of this, the calculated value of the work function Φ (5.05 eV) is in satisfactory agreement with the experimental value of 5.25 eV.[16] Since the corresponding values for the W(001) face are 4.3 eV (Ref. 1) and 4.63 eV (Ref. 16), respectively, the work-function difference between the two surfaces is reproduced well. As discussed in Ref. 12, the muffin-tin component of the potential is defined as being constant in the interstitial region of the crystal, spherically symmetric in the atomic spheres, and planar symmetric outside the surface. In Fig. 2, we show the variation of the self-consistent potential and its muffin-tin component for the W(110) surface for planes including nearest-neighbor (001) and next-nearest-neighbor (1̄12) surface atoms. The corresponding contour plots for the full potential are shown in Fig. 3.

The non-muffin-tin contributions to the potential are important, as we also found in the case of W(001). There is a pronounced corrugation parallel to the surface, and the shallow potential well evident in Fig. 2(a) is, of course, absent in the muffin-tin approximation. It is also interesting to see the obvious differences between the potential distributions found here and the corresponding results of Ref. 1 for the W(001) surface. This is also apparent when the full potentials in the two cases are averaged parallel to the surface (Fig. 4).

The general behavior of the averaged potential inside the crystal is very similar in the two cases. The average of the full potential lies below the average in the interstitial region, the difference between the two reflecting the different geometries. However, the potentials near the surface are significantly different. The more open W(001) surface results in a less attractive interstitial potential and, in agreement with the differences between the inner poten-

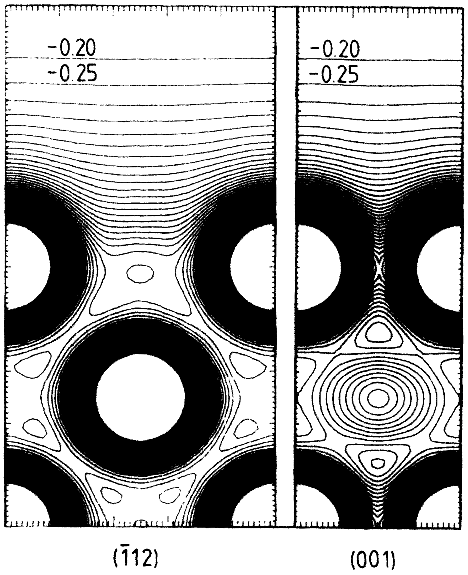

FIG. 3. Contour plot of the self-consistent potential in two planes perpendicular to the W(110) surface (see Fig. 1). The contours are marked in rydberg units and the interval is 0.05 Ry.

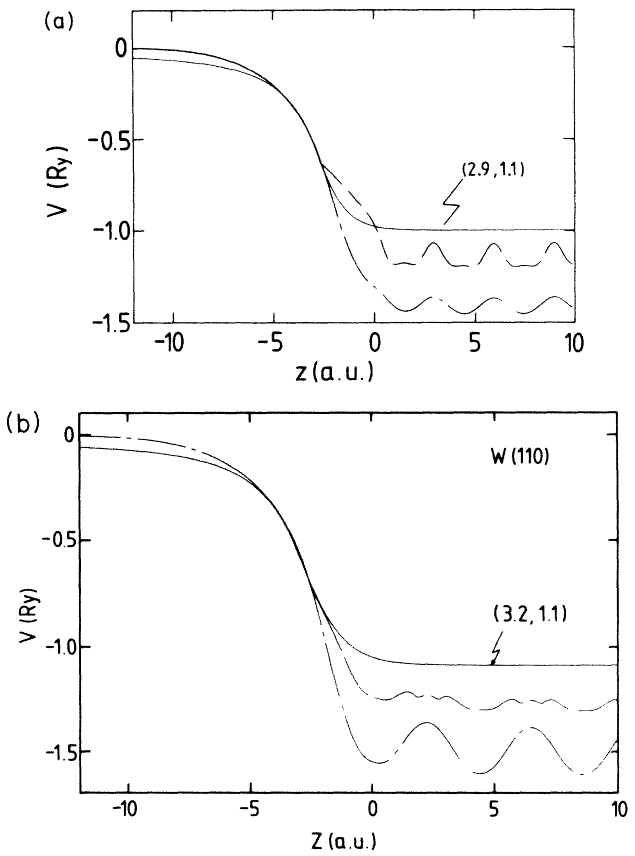

FIG. 4. Self-consistent potential averaged parallel to the surface in (a) W(001) (Ref. 1) and (b) W(110). The dashed-dotted curve corresponds to the full potential and the dashed curve for the region excluding the muffin tins. Also shown (solid curves) are barriers of the form of Eq. (1) with z_0, λ, and U_0 equal to (a) -2.9, 1.1, and 1.0, and (b) -3.2, 1.1, and 1.1 (rydberg atomic units).

tials[17] and work functions[16] for the two surfaces, the potential barrier is *larger* in W(110). If we fit the averaged barrier to a model barrier of form (1), Fig. 4 shows that the barrier origin $z_0 \sim -3.2$ a.u., i.e., farther from the outermost atomic layer than in W(001). In view of the larger inner potential, this should not be surprising.

III. ELECTRONIC STATES IN W(110) FILM

Holmes *et al.*[18] have reported a detailed analysis of the surface states (in the following we shall not distinguish between surface states and surface resonances) in W(110) using angle-resolved photoemission experiments. They were able to map out a surface state which extends over the whole of the SBZ. A five-layer film allows only very localized surface states to be identified unambiguously, and surface states on Ni(001) (Ref. 12) were identified in earlier work by "stretching" the film. This was done by subtracting the non-muffin-tin part of the potential and repeating the central layer potential. Calculations for the W(001) film,[6] however, showed that the state vectors changed appreciably when the non-muffin-tin part of the potential was neglected, and the procedure used for Ni(001) was not reliable. As a consequence, we have not attempted to stretch the W(110) film, and cannot estimate the dispersion of individual surface states.

Dense distributions of surface states may nevertheless be identified in the present calculations from the layer-projected densities of states (LPDOS), and these are shown for the surface (S), subsurface ($S-1$), and central layers ($S-2$) in Fig. 5. Note that these have not been broadened. The projections include only contributions from inside the muffin-tin spheres. The relative importance of the missing states may be estimated by subtracting the sum of the projected densities of states for all the layers from the total density of states, i.e., the one calculated from the band structure for the entire film. This difference density of states has the same structure as the total density of states, and was about one order of magnitude smaller in all cases. Since approximately 10% of states are uniformly missing in each LPDOS, the calculated values are good representations of the true LPDOS.

The LPDOS curves for the subsurface ($S-1$) and second layers below the surface ($S-2$) show pronounced similarities, and are also remarkably similar to the results for the W(001) surfaces (see Fig. 4 of Mattheiss and Hamann[5] and Fig. 4 of Posternak *et al.*[4]). The Fermi energy lies in a minimum in the pronounced d structure and the occupied d states are separated by another deep minimum around 4–5 eV below E_F. The surface PDOS shows some similarity to those for the W(001) surface. The lower d states are removed and some states are pushed up into the valley near -5 eV, forming surface states or resonances. The valley near the Fermi energy has disappeared at the surface due to the appearance of surface states. This is also similar to the (001) surface, even though the structure is broader and lower in Fig. 5. Two distinct surface-state peaks may be seen at -0.7 and -1.6 eV.

The projected surface densities of states published recently for W(110) resulted from model calculations which

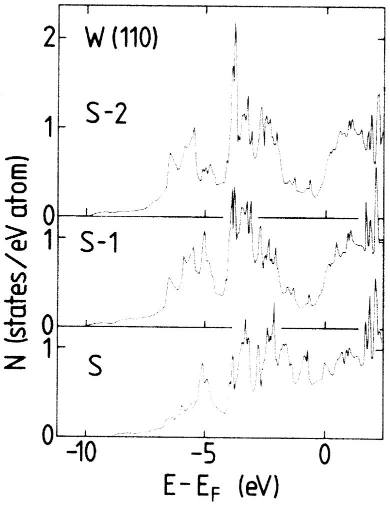

FIG. 5. Calculated densities of states for surface (S), subsurface ($S-1$), and central ($S-2$) layers of the five-layer W(110) film. The energy zero is at the Fermi energy.

were not self-consistent.[8,9] They bear only superficial resemblances to our results, and a detailed comparison seems inappropriate. A comparison with results for Mo is instructive, however, since the surface electronic structures of Mo and W are very similar. Noguera *et al.*[10] have calculated the surface density of states for Mo(110) and, although this calculation was also not self-consistent, the positions of the surface-state peaks are in good agreement with ours.

IV. DISCUSSION AND CONCLUSIONS

In the present paper, we have described self-consistent calculations of the electronic structure of a five-layer W(110) film. The densities of states for the different layers show similarities with previous calculations on W(001) and Mo(110), and provide information about the energy distribution of surface states.

The main focus of the present work has been, however, the spatial variation of the effective potential in the neighborhood of the surface (the surface barrier). The comparison between the W(001) and W(110) surfaces is of particular interest. The density-functional calculations give a satisfactory description of the surface anisotropy in the work function and the inner potential. Although potential variations on both surfaces show a pronounced three-dimensional character, the averages parallel to the surface can be reproduced well by a one-dimensional model barrier of simple form. The origin of the surface barrier, z_0, in W(110) lies approximately 0.3 a.u. farther from the outermost atomic layer than in W(001). Although this may have been anticipated from the larger inner potential on the (110) surface, it is the reverse of the prediction of Baribeau *et al.*[3] An analysis of the high-resolution LEED data is performed in the following paper.

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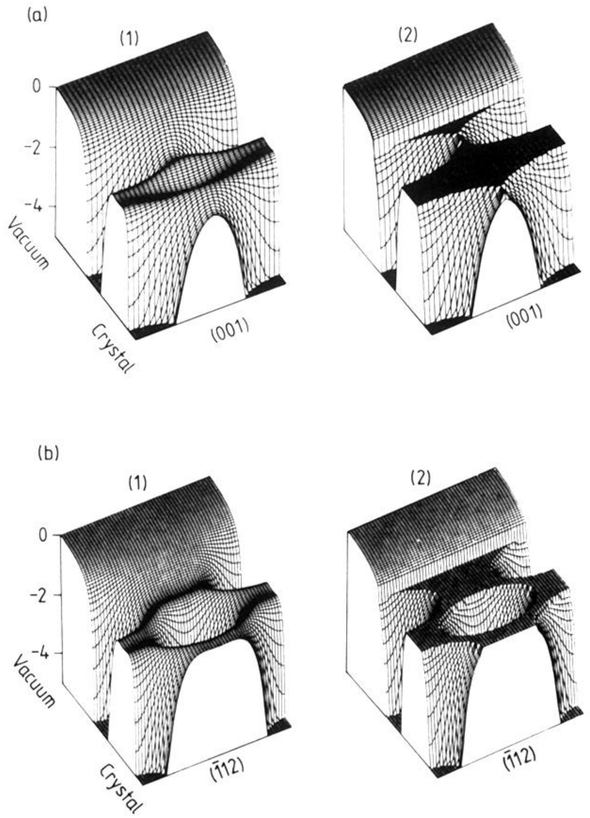

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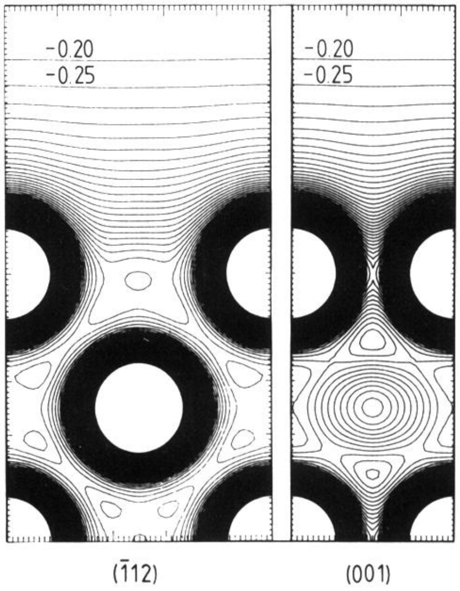

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