

Surface and interface states in the Cu/V(110) structure

S. B. Legoas* and B. Laks

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, CP 6165, 13083-970, Campinas, SP, Brazil

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We present *ab initio* calculations of the electronic structure of copper multilayers on V(110) surface. The calculations were based on density-functional theory and the real-space linear muffin-tin orbital method in the atomic-sphere approximation was used. Surface and interface states were investigated using the Green-function based transfer-matrix method. The results shown a variety of electronic states along the main symmetry lines of the two-dimensional Brillouin zone, and the presence of surface and interface states was verified. Also, the existence of a binding state about 1.8 eV below the Fermi level is in good agreement with recent photoemission experiments, such state can be interpreted as a quantum-well state.

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Recently the structure and properties of vanadium ultrathin films on Cu(100) were experimentally studied.¹⁻⁴ The measurements of Tian *et al.*² were interpreted as vanadium coverages having a body-centered tetragonal structure up to 6-7 monolayers (ML), while the results of Pervan *et al.*¹ and Waddill *et al.*⁴ shows a vanadium film having a four bcc-(110) domain structure at 2-3 ML. It was observed that this structure persists for V coverages as high as 100 ML, and the V in these films retain the bulk-V lattice constant. Similar four bcc-(110) domain structure was reported in the case of Cr and Fe ultrathin films on Cu(100).⁵⁻⁷ In all these cases the transition-metal film grows with its bulk-lattice constant, but the coverage thickness depends on the metal film considered. For Cr ultrathin films one notice a transition to the bcc Cr(110) structure starting from 3 ML, while for Fe the corresponding transition occurs with a coverage of no less than 10 ML.

It is well known that, upon annealing, copper diffuses on top of the transition-metal film.^{1,7-10} In the case of Cr, Fe, and V films it has been found that segregated copper follows the bcc-(110) structure of the underlying film.^{1,9} Thus Cu/M(110)/Cu(100) sandwich structures are expected to be formed when transition metal *M* ultrathin films deposited on Cu(100) surface are annealed.

In the annealing experiments of Pervan *et al.*¹ on V/Cu(100) system, it was observed a feature in the photoemission spectrum at about 1.8 eV below the Fermi level. In a more recent study of the structure and properties of copper ultrathin films on V(110) surface,¹¹ a very high-intensity peak at 1.8 eV was also observed for 2-ML film. The interpretation of the nature of this state was as being an *sp*-derived quantum-well (QW) state. As the copper films grow pseudomorphically up to 2-ML coverage, we were motivated to study the electronic structure of Cu/V(110) system, using our recently implemented method to study metal surface states,¹² using the real-space linear muffin-tin orbital method in the atomic-sphere approximation RS-LMTO-ASA,¹³⁻¹⁵ and the Green-function based transfer-matrix method.^{16,17} To our present knowledge, we do not know any other similar first-principles density-functional theory study on surface and interface states in metallic multilayers systems. The RS-LMTO-ASA scheme¹³ is based on the well-known LMTO formalism¹⁸ and uses the recursion

method¹⁹ to solve the eigenvalue problem directly in real space. The scheme has been extended to treat metallic surfaces.^{14,15} The transfer-matrix approach^{16,17} is a powerful method to calculate the spectral density of states for any given **k** vector in the two-dimensional (2D) Brillouin zone, at any of the slabs of atomic planes forming the solid with a surface. As the information provided by the spectral density of states is more complete than that contained in the local density of states, since we can look at a given momentum transfer parallel to the surface, we used this method in connection with the first-principle RS-LMTO-ASA to transform the real-space self-consistent Hamiltonian of the ultrathin film system provided by the RS-LMTO-ASA, into the reciprocal-space Hamiltonian along the desired 2D Brillouin direction. The spectral density of states is a relevant quantity for the analysis of, for instance, angle-resolved photoemission experiments.^{20,21}

In our calculations we used the local-density approximation for the exchange-correlation term of the potential energy, according to the von Barth and Hedin parametrization form.²² A nonrelativistic calculation was performed in a cluster of ≈ 3000 atoms, arranged in 11, 12, and 13 atomic planes parallel to the bcc-(110) surface, for the cases of clean vanadium surface, and one and two monolayers of copper on the vanadium surface, respectively. In all these cases, one empty spheres overlayer was considered, and in the self-consistent process showed to be sufficient consider up to five vanadium atomic planes. The same lattice parameter of 4.96 a.u. was used for vanadium and copper (110) planes, and the interplane distance was 4.05 a.u. for all the planes.

To better understand the effects caused by the copper overlayers on V(110) surface, we also present in this work the calculated results for the free vanadium (110) surface. In Fig. 1 we show the projected bulk band of vanadium in the [110] direction, and the surface states of V(110) system. We identify a surface state (labeled as V1) just below of Fermi level, about -0.27 eV at Γ point. This state is localized in the relative gap of the even projected bulk band of vanadium. Along the high symmetry $\bar{\Delta}$ direction this state goes up to $k_{\parallel}=0.5(\pi/a)$ with negligible dispersion. On the other hand, in the $\bar{\Sigma}$ direction the state goes up to $k_{\parallel}=0.4(\pi/a)$ with -0.75 eV. This electronic state is highly localized in the

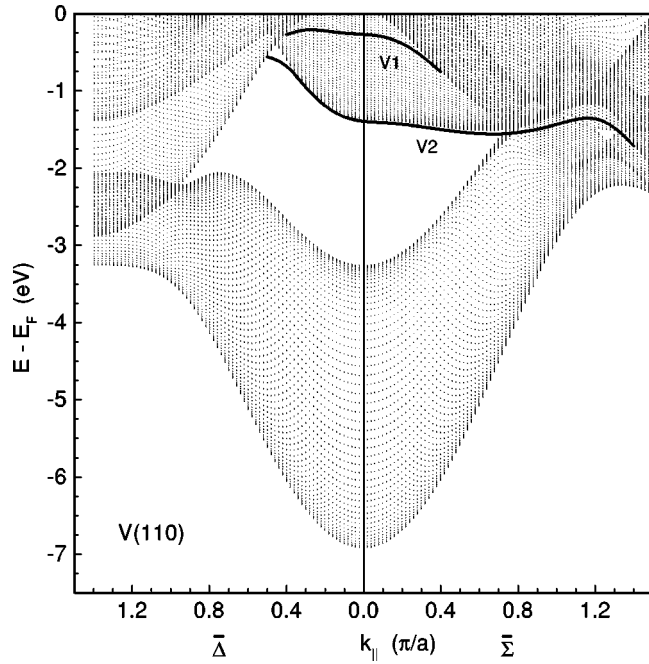


FIG. 1. Dispersion of surface states on V(110) along $\bar{\Delta}$ and $\bar{\Sigma}$ directions, and (110)-projected vanadium bulk band.

surface plane, with main orbital character being d_{z^2} . A second electronic state ($V2$) is obtained below the first surface state, with energy of -1.4 eV at $\bar{\Gamma}$ point. The behavior of this state is very different with respect to the state $V1$, and the main orbital character is d_{xy} . By this reason, the state $V2$ cannot be excited and detected in a photoemission experiment,²³ in opposite way to the state $V1$ that is observed in normal emission spectra.¹

In Figs. 2 and 3, we show our results for 1 ML and 2 ML of copper on the V(110) surface. For the case of 1 ML Cu (Fig. 2), it can be seen a number of states of different nature. First, we note the same states of vanadium ($V1$ and $V2$) as in Fig. 1. The state $V2$ shifted slightly toward the Fermi level, and decreased in the extremes, i.e., it survives in a short region of the 2D Brillouin zone. The state $V1$ has experienced a major modification, particularly in the $\bar{\Sigma}$ direction, since their extension is now up to $k_{\parallel}=0.2(\pi/a)$. This state has shifted 0.18 eV at $\bar{\Gamma}$ point toward the Fermi level. Clearly, this behavior is due to the interaction with the copper overlayer. In Fig. 2 we note the effect of 1-ML copper coverage, with the presence of a number of $3d$ -like states. In first place we observe the state labeled as $C1$, an almost s -like state, with predominantly orbital character $d_{x^2-y^2}$ at the 2D Brillouin zone extremity. This state, localized in the copper plane, with minor occupation in the first vanadium plane, is on the beginning of the (110) projected bulk band of bcc Cu (not shown here), and it will shift to more negative energies as long as more copper overlayers will be considered over the vanadium (110) surface (to be seen in Fig. 3). Similar behavior is observed in the case of states $C2$, $C3$, and $C4$, namely, they have even symmetry and will shift down to the bcc-Cu bulk band. All the copper states (labeled with C) are mainly localized in the copper overlayer, and in

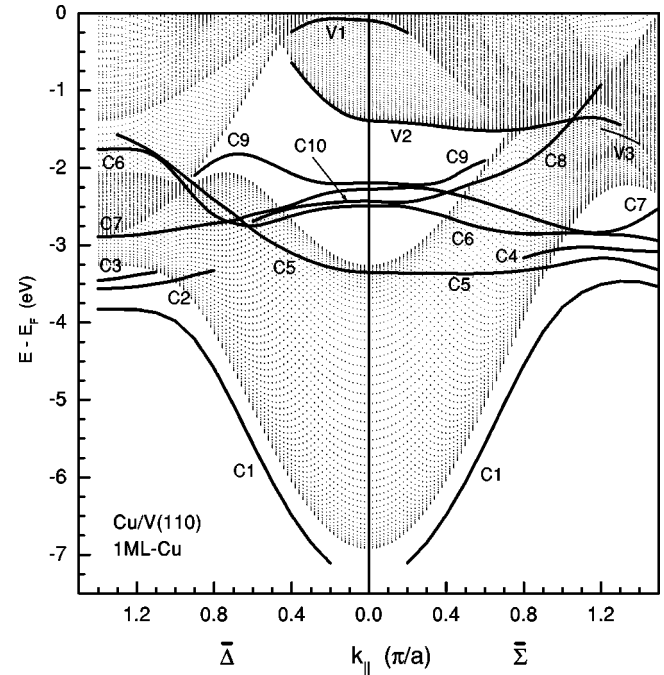


FIG. 2. Dispersion of surface states on Cu/V(110), with 1 ML of copper, along $\bar{\Delta}$ and $\bar{\Sigma}$ symmetry lines. The states labeled as $V2$, $C5$, and $C10$ have odd symmetry, while all the other states have even symmetry. The states $V1$, $V2$, and $V3$ are localized into the first two vanadium planes, and the other states are mainly confined into the copper plane.

minor concentration in the first vanadium plane, except the state $C5$ that is localized only in the Cu plane and has d_{xy} as orbital character. We note that all the 1-ML copper states act in this case as being surface states, but only some of them, around the $\bar{\Gamma}$ point and between -3 and -2 eV, will really stay in a relative gap, in this case, the relative gap of the even (110) projected vanadium bulk band. So, strictly speaking, only the states $C6$, $C7$, $C8$, and $C9$ will be considered as surface states, meanwhile the other states we denote as being *pseudosurface states*. These *pseudosurface states* can be observed in ultraviolet photoemission (UP) spectroscopy.¹¹ It is interesting to note that above -2 eV at $\bar{\Gamma}$ there is no copper states, and in this case no feature will be observed in the experiment.¹¹

The most striking features are observed for the case of two copper ML at vanadium (110) surface (Fig. 3). In Fig. 3(a) we show our results for the states of even symmetry along $\bar{\Delta}$ and $\bar{\Sigma}$ main symmetry lines, and the even (110)-projected vanadium bulk band. In Fig. 3(b) are shown the odd-symmetry states, as well as the odd (110)-projected bulk band of vanadium. In Fig. 3(a) we observe the same vanadium state $V1$, with some modifications, that shifted toward the Fermi level and now has an energy of -0.03 eV at $\bar{\Gamma}$ point. The same behavior is also observed in the case of the odd-symmetry state $V2$ [Fig. 3(b)]. From Fig. 3(a) we identify some *pseudosurface states* as in Fig. 2, that is, the states $C1$, $C2$, $C3$, $C4$, and $C5$. It is easy to verify that these states shifted down about 0.2 eV, and they are localized in the second copper plane (the interface copper plane), with little

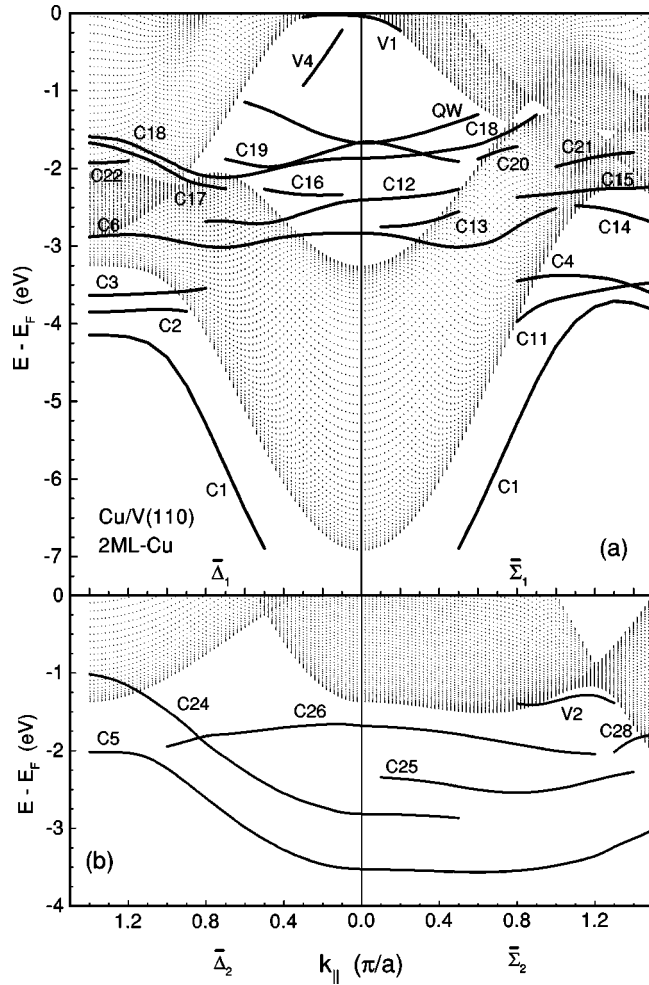


FIG. 3. Dispersion of even- and odd-symmetry states on Cu/V(110), with 2 ML of copper, along the main symmetry directions. The projected even- and odd-symmetry vanadium bulk bands are also shown. The vanadium lattice parameter is $a = 3.03 \text{ \AA}$.

contribution of the first copper plane (the surface copper plane, in this case). Certainly, these states will transform in bulk states of bcc Cu as the number of copper planes increase significantly. Clearly, a number of new states have appeared as a second copper monolayer has been deposited on vanadium (110) surface. The major part of them are confined in the surface copper plane, with minor contribution of the interface copper plane, except the states C11, C12, and C16 that are localized in the interface copper plane. Here we have to indicate that a second type of state has emerged in response to the presence of a second deposited copper plane. We denote these states (C11, C12, and C16) as being *interface states*. In this context, the states V1 and V2 can also be considered as being *interface states* in as much as they are confined in the first two vanadium planes (interface vanadium planes). In addition to the copper interface states (C12 and C16), which are localized in the even relative vanadium gap between -3 and -2 eV, we identify three more new states above the -2 eV level. They are the states labeled as C18, C19, and QW. The first two are copper surface states, localized in the even relative vanadium gap, and in the $\bar{\Gamma}$

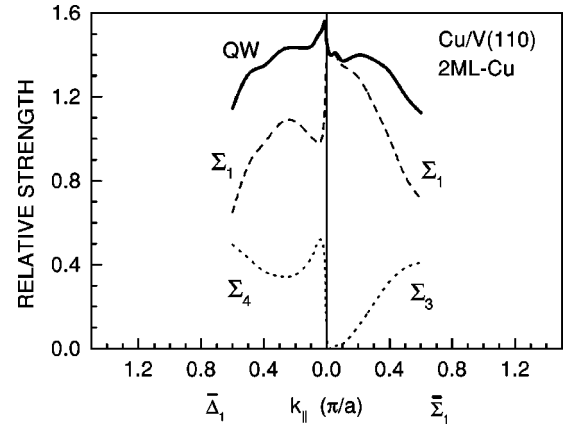


FIG. 4. Relative surface local density of states (SLDS) of the quantum-well (QW) state on Cu/V(110) with 2 ML of copper, along the main symmetry lines. In the SLDS is considered the contribution of the first three planes (surface and interface copper planes, and interface vanadium plane). The orbital components of the QW state are also shown.

point these states have mainly Σ_4 and Σ_3 symmetry. By this reason these states could be excited only by *s*-polarized light.²³

The last new state created by the deposition of a second copper plane on vanadium (110) surface, is the state labeled QW. This state, localized in the even relative vanadium gap, has an energy of -1.7 eV at the $\bar{\Gamma}$ point. Their dispersion is similar to the feature observed in the UP spectra of an ordered 2-ML Cu film on V(110) (labeled as b_2 in the work of Kralj *et al.*¹¹). The QW state is composed mainly by orbitals of $\bar{\Sigma}_1$ symmetry, and by this reason this state could be excited by *p*-polarized light, as well as by *s*-polarized light. This state is confined mainly in the first three planes (surface and interface copper planes, and interface vanadium plane), and therefore it has not evanescent character, by all these reasons we identified the QW state as being the feature observed at 1.8 eV below the Fermi level in normal emission, as shown in the work of Kralj *et al.*¹¹ In Fig. 4 is shown the behavior of the density of states of the QW state along the main symmetry lines. It was considered the contribution of the first three planes where the state is confined. It can be observed a major concentration of states around the $\bar{\Gamma}$ point, in accordance with photoemission experiments.¹¹ It is also noted the distribution of the orbitals by their symmetry. Clearly, the symmetry $\bar{\Sigma}_1$ is the main character in the QW state, specially around the $\bar{\Gamma}$ point. By the fact the QW state appears with 2 ML of copper on vanadium surface, and be confined mainly in the first three planes (with a minor contribution of the fourth plane, but with negligible contribution of the other vanadium planes), we identified this state as being a quantum-well state, as was stated by Kralj *et al.*¹¹

In Fig. 3(b) we shown all the odd-symmetry states that appear below the odd (110)-projected vanadium bulk band. The state V2 of vanadium is still present, however, the extension of this state was shortened significantly, remaining only in the $\bar{\Sigma}_2$ direction. This behavior is explained considering that the effect of the copper planes on vanadium (110)

surface on the states $V1$ and $V2$ is to shift these states toward the Fermi level. As the state $V2$ exists very near of the bottom boundary of the odd projected vanadium bulk band, any significant shift of the state toward the Fermi level provokes its overlapping with bulk states of vanadium, and as a consequence the state $V2$ will lose their surface state character, and will be then part of the bulk continuous. Only the right part of the state $V2$ will still remain out of the vanadium bulk, and by this reason in the 2ML Cu situation the state $V2$ will be as shown in Fig. 3(b). As was stated before in the case of the even-symmetry states, we identified a state $C25$ as being an odd interface state as well as the state $V2$. The states $C5$ and $C7$ are the same as in Fig. 2, while $C24$, $C26$, and $C28$ are odd pseudosurface states.

In conclusion, we have carried out first-principles calculation of the electronic structure of Cu/V(110) multilayers system, using our recently implemented scheme¹² that combines the surface RS-LMTO-ASA approach with the Green-function based transfer-matrix method, to analyze the surface states structure of ultrathin film metallic systems. We obtained striking states structures along the main symmetry lines, in the case of 1 ML and 2 ML of copper on vanadium (110) surface. It was shown that in the case of 1 ML of

copper, no states are present above -2 eV, except the vanadium (110) surface states. On the other hand, when a second copper plane is considered on the vanadium (110) surface, we identified a number of new copper states, that explain the structure observed in photoemission experiment in the range of -3 to -2 eV. Finally, our results show the existence of a state localized at 1.7 eV below the Fermi level at $\bar{\Gamma}$ point, which is identified as being a quantum-well state, as was stated by Kralj *et al.*¹¹ The main orbital character of this QW state is of Σ_1 symmetry, and so it will be mainly excited by p -polarized light.

For completeness sake, we also investigated possible relaxation effects on the surface states dispersion relations. In this study we considered that the interplane distances related to the first three layers go from -2 to -4% , respecting to the bulk interplane distance. Our results showed the stability of the surface states pattern. The main observed effect was just an energy shift no greater than 0.06 eV (at $\bar{\Gamma}$ point).

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*Corresponding author. FAX: +55-19-37885376. Electronic address: slegoas@ifi.unicamp.br

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