Two-dimensional localization of fast electrons in $p(2\times2)$-Cs/Cu(111)

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The system $p(2\times2)$-Cs/Cu(111) reveals a manifold of surface localized electronic states, such as image states, quantum well states, and surface resonances. We find an electronic state with a band energy above the vacuum level while strictly localized at the Cs monolayer. An electron populating this state will have a large in-surface-plane kinetic energy and, presumably, a very long lifetime. The state could be an interesting tool for control of electron induced surface reactions.

PACS number(s): 73.20.−r, 71.15.Mb, 71.20.−b, 73.21.Fg

Adsorption of alkali atoms on simple and noble metal surfaces has for a long time been considered as bench mark models for metal adsorption. During the recent past two decades, experimental[1,2] and theoretical[3–6] studies have shown that the alkali-on-metal adsorption system is far more complex and rich with electronic properties than expected.

It is well known from experiments and theory that the (111) surface of noble metals exhibits a local band gap perpendicular to the surface hosting surface localized electronic states. The state with the lowest energy is referred to as the surface state, and the sequence of bands with less binding energy is the image state series. Electrons occupying surface states close to the Fermi level extend far toward vacuum and, therefore, play an important role in the adsorption of weakly physisorbed species.[7,8] Unoccupied image states may be important for hot electron transport at surfaces. For surface states and image states appearing in the surface projected directional gap, the lifetime broadening, determined by inelastic processes due to electron-electron and electron-phonon scatterings, is found to be in the range of 1–50 meV.[9] This corresponds to lifetimes in the range of 0.01–1 ps.

Adsorption of alkali overlayers introduces a significant change in the electronic structure of the surface. Charge transfer from the alkali layer to the metal reduces appreciably the work function and new states appear at the interface, such as quantum well states (QWSs) and overlayer resonances (ORs).[10] The lifetime of these states will depend on the amount of both elastic (coupling to bulk bands) and inelastic scattering processes.

In this Brief Report, we demonstrate the existence of a, not previously discussed, one-electron gap state (GS) found for the system of a full monolayer of Cs on Cu(111). Outstanding characteristics of the GS are (i) a band energy well above the vacuum level, (ii) appearance in a local bulk band gap but within the continuum of vacuum states, (iii) strong localization to the Cs layer, and (iv) large in-surface-plane component of the kinetic energy. An electron excited to this state will travel fast parallel to the surface being strictly confined within the Cs layer. Control of electron induced reactions of atomic species decorating surface terrace step edges is a possible application—a nanoscale electron gun.

The electronic structure calculations are based on the density functional theory. We have applied two different (ultrasoft pseudopotentials) plane-wave codes[11] and a Green's function based embedding scheme[12] within a full potential linearized augmented plane-wave approach. All of them make use of the generalized gradient approximation for the exchange and correlation energy functional.[13]

To obtain the ground state atomic structure of $p(2\times2)$-Cs/Cu(111), we used the PWSCF code[14] and a slab of ten layers of Cu atoms with double-sided adsorption of the Cs atoms and 24 Å of vacuum. The Cu atoms were allowed to relax in any direction and the Cs atom, in the on-top[15] position, in the direction perpendicular to the Cu planes. Our determination of the relaxed geometry agrees well with experiment.[16]

For a detailed investigation of the surface electronic states, we take advantage of the embedding scheme.[6] In this scheme, the Cs overlayer and the two topmost copper layers are considered in the calculation. The correct matching with the vacuum and bulk solutions is guaranteed by a nonlocal energy-dependent potential acting on the boundaries of the embedded region. This extended substrate approach allows one to properly take into account the continuum of bulk states and consequently the presence of the resonances and their elastic width, if any.

The electronic structure of $p(2\times2)$-Cs/Cu(111) reveals a variety of surface features: Overlayer resonance, quantum well state, image states (ISs), and gap state. In Fig. 1, we show the calculated band structure, applying the embedding scheme, along the $\overline{\Gamma M}$ path. In such a method, the semi-infinite character of the substrate (i) prevents the appearance of surface localized band doublets, as in the case of finite slab calculations, and secondly, (ii) allows the determination of the inherent elastic width of states.

The $p(2\times2)$ periodic perturbation introduced by the Cs layer yields folded copper bulk bands which reduce appreciably the projected band gap of Cu(111).[4] As a result of this folding, hybridization of surface localized states takes place, which gives elastic widths to the bands. We find that the elastic width of the QWS (shown in Fig. 1) increases from 2.4 meV in the $\overline{\Gamma}$ point to 35.4 meV halfway out to the $\overline{M}$
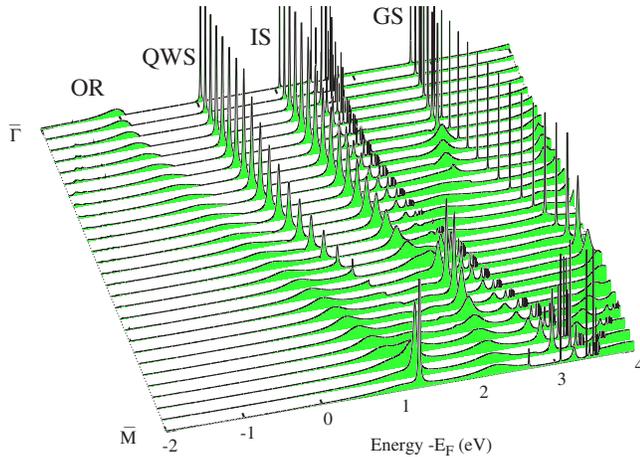
FIG. 1. (Color online) Cs/Cu(111) $\mathbf{k}_\parallel$-resolved local density of states along the $\overline{\Gamma M}$ path in the SBZ. The local density of states has been integrated over the vacuum volume.

point. The minimum of the parabolic band centered at $\overline{\Gamma}$ is slightly above the Fermi level ($\sim$40 meV), which is in agreement with a recent theoretical and experimental scanning tunneling spectroscopy study.[4] As described below, other states such as image states and the overlayer resonance, shown in Fig. 1, with energies below and above the QWS are found to have elastic widths at $\overline{\Gamma}$ significantly larger or comparable to the QWS, respectively. At $\overline{\Gamma}$, an exceptionally sharp feature is found above the vacuum level in the projected bulk band gap. This gap state, analyzed in detail below, is the focus of this Brief Report.

A new method has been proposed[6] to merge the Kohn-Sham potential asymptotically far from the surface into the correct image form $-1/4z$. Implementation of this method in the embedding scheme has made it possible to determine the (ISs). The manifold of the parabolic IS bands are shown in Fig. 1, with an energy at the $\overline{\Gamma}$ point of 1.04, 1.46, and 1.60 eV above the Fermi level for the lowest three states.

The OR band is located about 1.2 eV below the Fermi level at the $\overline{\Gamma}$ point which is in agreement with recent reported photoemission data.[10] The broad feature of this band reflects its resonance character, as clearly seen in Fig. 1. The wave function at the surface Brillouin zone (SBZ) center, presented in Fig. 2(a), also shows the resonance behavior with a persisting oscillation (nonexponential decay) into the slab.

In addition to these bands, we observe an interesting, and to our knowledge not previously analyzed, Cs induced band (GS) which meets the $\overline{\Gamma}$ point in a bulk band gap at about 2.7 eV above the Fermi level. As the calculated and experimental work function of the system is 1.8 eV, the GS is located 0.9 eV above the vacuum level in the SBZ center. Still, the planar averaged wave function squared at the SBZ center is surprisingly localized to the Cs layer [Fig. 2(c)]. This localized character is consistent with zero width calculated applying the embedding scheme. As it is shown below, the reason for this localization is that the main part of its one-electron energy is attributed to kinetic energy parallel to
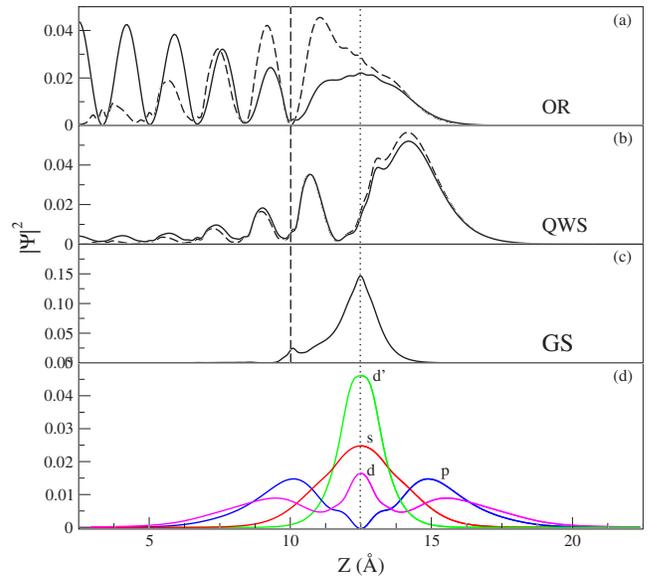

FIG. 2. (Color online) Planar averaged squared magnitude of wave functions at the $\overline{\Gamma}$ point. (a) Even (solid line) and odd (dashed line) of the OR, (b) even (solid line) and odd (dashed line) of the QWS, (c) GS, and (d) s, p, d, and d' bands of the unsupported Cs layer. The vertical lines correspond to the outermost Cu atom layer (dashed) and the Cs layer (dotted). Zero on the horizontal axis is the middle of the slab.

the surface. As the GS band has zero elastic width despite its energy position in the continuum of vacuum states, the inherent width should thus be due to the inelastic processes, such as electron-electron and electron-phonon scatterings.

The origin of the GS band, as well as the OR and QWS bands, can be understood from the band structure of the free-standing Cs monolayer. Referring to Figs. 2 and 3, we can associate the lowest band s with the OR band, the p band with the QWS band, and the folded s band, labeled d', with the GS band. In Fig. 1, we see the gap opening at the $\overline{M}$ point
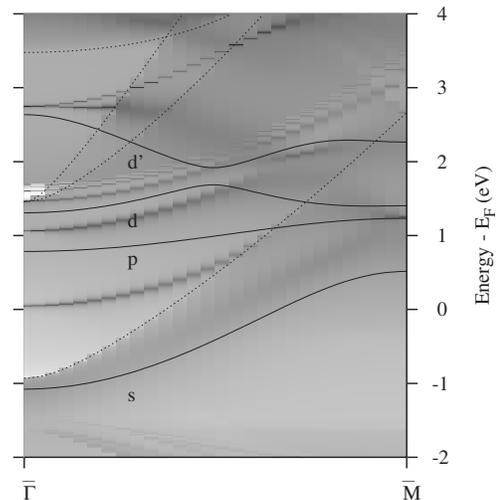

FIG. 3. Band structure of Cs/Cu(111) and unsupported Cs layer. The unsupported Cs layer bands (s, p, d, and d') are denoted by solid lines. The dotted lines show the bulk band edges due to folding.

(as for the unsupported Cs layer between the s and the d' band, as seen in Fig. 3). This band gap opening is not present at the $\bar{K}$ point both for the unsupported Cs layer[17] nor for the adsorbed Cs layer (not shown). The reason is that along the $\bar{\Gamma}\bar{M}$ direction, the Cs nearest neighbor (nn) distance is about twice the nn distance in the $\bar{\Gamma}\bar{K}$ direction and, thus, the one-electron potential is more corrugated in the $\bar{\Gamma}\bar{M}$ direction.

The band corresponding to the d band for $p(2\times2)$-Cs/Cu(111) is not seen in Fig. 1 in the region from the center to about halfway out to the SBZ boundary. This is due to the fact that the potential is too shallow to form this bound state. This is indicated by the lower work function for Cs/Cu(111) than for the freestanding Cs layer, 1.8 eV in comparison with 2.21 eV, respectively.

Furthermore, if we compare the wave functions of the freestanding Cs monolayer with the ones for Cs/Cu(111) at the $\bar{\Gamma}$ point (Fig. 2), we have additional support for this picture. In the SBZ center, the wave functions of s, d', OR, and GS have no nodes in the Cs layer, while the p and QWS band has one node. The pronounced confinement of the GS to the Cs layer is also seen for the corresponding d' state wave function for the unsupported Cs layer. The reason for the even stronger localization compared to the s band state is due to the strong hybridization with the d band which, in turn, is responsible for the avoided crossing of the bands forming lower bonding and upper antibonding bands, d and d' (see Fig. 3), respectively.

Our calculated band structure of the unsupported Cs monolayer is similar to the one obtained by Wimmer,[17] who symmetrically analyzed the bands. He concludes that the symmetry of the d and d' bands is the same, which is consistent with the observed avoided crossing phenomenon. The avoided crossing phenomenon persists for $p(2\times2)$-Cs/Cu(111) halfway between $\bar{\Gamma}$ and the SBZ boundary, as shown in Fig. 1.

It is interesting to note that both the PWSCF and the embedding scheme yield the same GS energy, 2.7 eV above the Fermi level, and the same Cs layer localized wave function, as pictured in Fig. 2(c). The embedding scheme calculation yields the correct asymptotic image form of the self-consistent one-electron potential, while PWSCF does not. However, this is not an important issue for the GS which is well localized to the Cs layer plane. However, what is the origin of the localization? We conclude that the GS band is a Cs induced band and analyze now further the character of the GS band in the $\bar{\Gamma}$ point.

Due to the fact that the GS appears as a folded OR state, we expect that a substantial part of the GS band energy in the $\bar{\Gamma}$ point is attributed to parallel kinetic energy. Applying the free electron empty lattice model, the parallel contribution to the total GS energy is $\epsilon_{\parallel}^{GS}=\hbar^2|\vec{G}_1|^2/2m=7.41$ eV, where $\vec{G}_1$ is the shortest reciprocal lattice vector parallel to the surface. However, the gap opening at the $\bar{M}$ point signals a periodic potential in the Cs layer, and thus we cannot trust this estimate. If the potential is not strictly sinusoidal, we would also have contributions from larger reciprocal lattice vectors to the GS wave function. From the calculated self-consistent GS wave function, we can obtain the expectation value of the parallel kinetic energy,
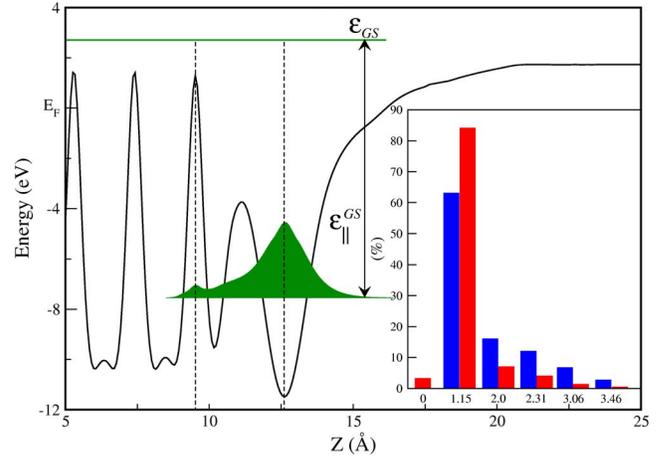

FIG. 4. (Color online) Planar averaged v_{SCF} (solid line) and the squared magnitude of the GS wave function [green (gray)]. The energy of the GS when subtracting the calculated $\epsilon_{\parallel}^{GS}$ is indicated by the vertical arrow. The histogram shows the squared magnitude of the GS wave function [red (gray)] and parallel kinetic energy [blue (dark gray)] resolved in terms of contribution from different parallel reciprocal lattice vectors $\vec{G}_{\parallel}$. The horizontal axis shows $|\vec{G}_{\parallel}|$ in units of $2\pi/a$, where $a=5.2$ Å is the nearest Cs-Cs distance in the Cs layer.

$$\epsilon_{\parallel}^{GS}=-\frac{\hbar^2}{2m}\langle\psi_{GS}|\vec{\nabla}_{\parallel}^2|\psi_{GS}\rangle, \tag{1}$$

where $\vec{\nabla}_{\parallel}^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}$ and ψ_{GS} is the *first principles* gap state wave function. At the $\bar{\Gamma}$ point ($\vec{k}_{\parallel}=0$), the GS wave function can be written as

$$\psi_{GS}(\vec{R},z)=\sum_{\vec{G}_{\parallel},g}C_{\vec{G}_{\parallel}g}e^{i\vec{G}_{\parallel}\cdot\vec{R}}e^{igz}, \tag{2}$$

where $\vec{R}=(x,y)$ and $\vec{G}_{\parallel}$ and g are the parallel and perpendicular components of the reciprocal lattice vectors $\vec{G}=(\vec{G}_{\parallel},g)$. We then have

$$\epsilon_{\parallel}^{GS}=\frac{\hbar^2}{2m}\sum_{\vec{G}_{\parallel},g}|\vec{G}_{\parallel}|^2|C_{\vec{G}_{\parallel}g}|^2=10.34 \text{ eV}. \tag{3}$$

Subtraction of this energy from the band energy of the GS is illustrated in Fig. 4. The free electron estimate was 7.41 eV, which is about 72% of the 10.34 eV. This is approximately in agreement with our findings when resolving $\epsilon_{\parallel}^{kin}$ in terms of its contributions from different parallel reciprocal lattice vectors. From the histogram in Fig. 4, we observe that only about 63% of $\epsilon_{\parallel}^{kin}$ originates from the shortest $\vec{G}_{\parallel}$ vector and thus 37% from higher order diffraction.

The contributions from the different $\vec{G}_{\parallel}$ can be understood from the x,y plot of the GS wave function, as shown in Fig. 5. The Cs next-nearest-neighbor direction corresponds to the magnitude of the shortest reciprocal lattice vector $|\vec{G}_1|$, the nearest-neighbor distance to the next smallest $|\vec{G}_2|$, and the
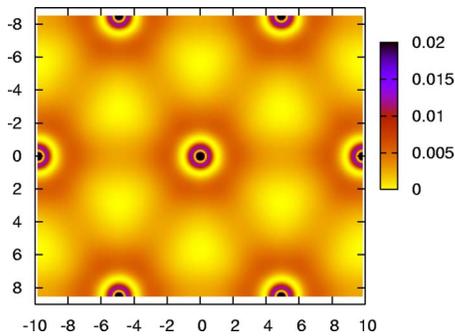
FIG. 5. (Color online) Electron density map of the gap state in the plane parallel to the surface intersecting the Cs layer.

third $|\vec{G}_3| = 2|\vec{G}_1|$ related to the shorter wave length corrugation seen in the next-nearest-neighbor direction.

In conclusion, we find a different kind of electronic state, denoted as gap state, located in the projected bulk band gap which (i) have a band energy above vacuum level, (ii) is spatially localized at the surface, (iii) have a large in-surface-plane kinetic energy, and (iv) is expected to have an exceptionally large lifetime in the range of $0.1-1$ ps due to inelastic scattering by phonons or electrons. The estimated lifetime yields an electron traveling-distance parallel to the surface of $500-5000$ Å. We propose that when the GS is populated by means of photon absorption or electron injection in a STM or inverse photoemission setup, an electron strictly confined to the Cs overlayer moving fast parallel to the surface is present. A possible application is control of electron stimulated reactivity of reactants decorating edges of single crystal terraces of the alkali overlayer.

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