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Image potential states of supported metallic nanoislands

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Our theoretical study shows how well-resolved image potential states develop on metal-supported metallic nanoislands. The systems under consideration are one monolayer high Na nanoislands on the Cu(111) surface. However, the phenomenon is general and it requires only that the work function of the adsorbate is lower than that of the substrate, and that the substrate possesses a projected band gap along the surface normal.

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Creating nanostructures at surfaces provides an exciting opportunity of modifying and designing surface-specific states in a controlled way, where the range of possible applications extends from molecular electronics and surface reactivity to photonics. The two-dimensional (2D) states localized at and propagating along the surface [e.g., surface electronic states at the (111) surfaces of noble metals or surface plasmon-polariton] can be guided, trapped, or focused at the nanostructured surface.[1,2] Quantum corrals represent spectacular examples of confinement of surface localized states because of scattering at the boundaries of the artificially built structures.[1,3,4] Not only the nanostructure modifies the states which are already present at the surface, but new nanostructure-specific states can also emerge as has been demonstrated for, e.g., adatom chains,[5] nanoislands,[6] and adlayer structures.[7,8]

Presently, the phenomena controlling the properties of confined states are rather well understood leading to their quantitative descriptions.[4,9,10] The energies of the states are found to follow the general trends predicted by the "particle in a box" picture and their lifetimes are determined by the scattering at the boundaries of the confining structure. However, the very existence of the different confined states, or "what is the minimum size of the nanostructure for the various confined states to be observed?" is still an open question.

In this Rapid Communication, using one monolayer (ML) high Na nanoislands on the Cu(111) surface as an example, we show how localized image-potential states (ISs) develop on metal-supported metallic nanoislands. We observe that well-resolved ISs emerge for nanoislands as small as 7 Na atoms. For larger nanoislands series of localized ISs are formed corresponding to the quantization of the electron motion parallel to the surface because of the finite size effects.

For metal surfaces with projected band gaps ISs appear because an excited electron is trapped in front of the surface by the interaction with the self-induced polarization charge.[11] At a large distance z from the surface, this interaction corresponds to the classical image potential $V_{im}=-1/4z$ (atomic units) so that a hydrogenlike series of ISs is formed. The electron in an IS is bound in the direction perpendicular to the surface and propagates quasifreely parallel to the surface with an effective mass $m^* \approx 1$.[12] Being stationary within the one-electron picture, ISs decay primarily due to inelastic interactions with substrate electrons.[13] While the dynamics of ISs is well-studied for flat surfaces,[12,14] or for surfaces with adlayers or disordered adsorbates,[12,15–17] much less is known about ISs localized at nanostructures at surfaces. To the best of our knowledge, the only systems studied so far are Ar nanoislands on the Cu(100) surface.[18]

We address the nanoisland localized ISs in metal-adatom-island–metal-substrate systems by studying excited electronic states of small 1 ML high Na adatom islands deposited on the Cu(111) substrate. Na islands in the second ML of Na on the Cu(111) surface have been observed in a number of studies,[19,20] but it is argued that hexagonal-shaped Na islands could also be formed in the first ML on top of the close-packed (111) surface.[21] An extended description of the method including the choice of the nanoisland geometry and computational details can be found in our previous work.[22] Here we only briefly outline the theoretical approach based on the *ab initio* density-functional (DFT) calculations and the time-dependent wave packet propagation (WPP) study.

Self-consistent DFT calculations are carried out in the local-density approximation. The substrate is represented by a slab comprising 21 Cu(111) layers. The electron-Cu substrate interaction is described by a pseudopotential derived from the model one-dimensional potential $V_S(z)$ proposed by Chulkov *et al.*[23,24] The above potential choice allows us to incorporate the long-range image potential tail and leads to the correct description of the electronic structure of the Cu(111) surface at the $\bar{\Gamma}$ point including the projected band gap between −5.83 and −0.69 eV, the surface state at −5.27 eV, and the first IS at −0.82 eV (all energies are given with respect to the vacuum level). The 1 ML high (h=5.5 a.u., Ref. 20) completed hexagonal Na ad-islands are described by the cylindrical jellium model. We have studied islands comprising N_{Na}=7, 19, 37, and 61 Na atoms with the jellium cylinder radii R_{Na}=10.15, 16.72, 23.33, and 29.96 a.u., respectively.

The effective one-electron potential obtained from the DFT calculations is the input for the WPP study where the time-dependent Schrödinger equation for an "active" electron is solved on a grid in cylindrical coordinates. The quantization z axis is perpendicular to the surface and going through the center of the island. Because of the cylindrical

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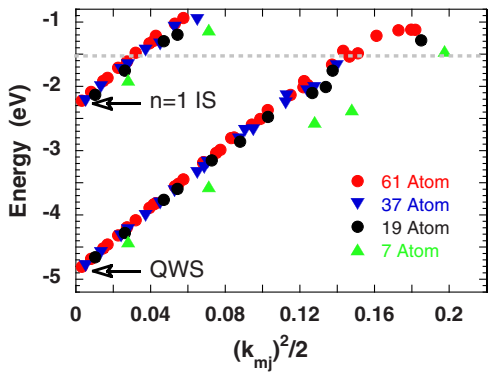

FIG. 1. (Color online) Energy of various (m,j) states for Na atom nanoislands on Cu(111). The energy is referred to the Cu(111) vacuum level. Results are shown as a function of the quantized wave vectors of the corresponding "particle in a box states" (see text for definition). Different symbols represent the states corresponding to the Na islands of different size, as shown in the inset. The dashed gray line shows the position of the vacuum level for the 1 ML Na/Cu(111) system.

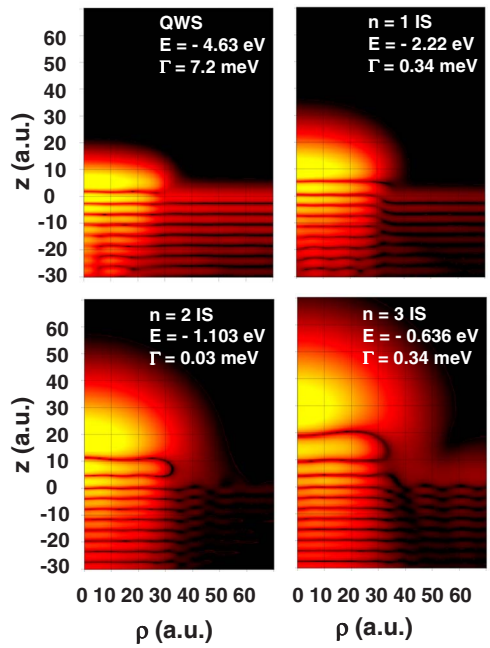

FIG. 2. (Color online) Interpolated images of the electron density of the $(m=0, j=0)$ quasistationary island-localized states for the 61 Na atom island on the Cu(111) surface. The states are labeled according to their parent continua. The natural logarithm of the density is shown in cylindrical coordinates. $z=0$ corresponds to the position of the image plane of the Cu(111) surface, and inside the metal z is negative. The vacuum edge of the Na island is at $z=5.0$ a.u. The electron density decreases from 1 to 0.001 (arbitrary units) when going from bright to dark. The energies E [with respect to the vacuum level of Cu(111)] and the widths Γ of the states are given in the insets.

symmetry, calculations are performed independently for each m subspace, where m is the projection of the angular momentum on the quantization axis. Absorbing potentials are introduced at the WPP mesh boundaries so that the calculation is free from finite slab effects. From the WPP we extract the properties (wave functions, energies E, and widths Γ) of the quasistationary island-localized states. The lifetime of the state against one-electron decay into the substrate is given by $1/\Gamma$.

We have first calculated the electronic structure of the 1 ML Na/Cu(111) surface. Present results compare well with available experimental and theoretical data.[7,20,25,26] Thus, at $\bar{\Gamma}$, the 1 ML Na on Cu(111) exhibits a quantum well state (QWS) at −127 meV below the Fermi level and a series of ISs with energies $E_{n=1}=-992$ meV, $E_{n=2}=-215$ meV, and $E_{n=3}=-90$ meV with respect to the vacuum level. Here, the ISs are labeled by their principal quantum number n. The entire ISs series is in the projected band gap of Cu(111) because of the −1.53 eV shift of the vacuum level as induced by the Na monolayer. Both the QWS and the ISs correspond to 2D continua of electronic states with an electron located inside the Na layer (QWS) or in front of its surface (ISs) and moving parallel to the surface. Suppose that instead of a complete Na monolayer we have a cylindrical nanoisland of radius R_{Na}. If the potential in the region of the island is the same as for the 1 ML Na/Cu(111), and if the island boundaries are 100% reflecting for the 2D electron, the QWS and ISs continua become quantized. A discrete series of island-localized states emerges with energies given by[22] $(m^*=1)$:

$$E_{m,j} = E_0 + k_{m,j}^2/2, \tag{1}$$

where j is an integer, E_0 is the energy of the corresponding parent continuum at $\bar{\Gamma}$, and the quantized electron wave vector parallel to the surface is $k_{m,j}=R_{m,j+1}/R_{\mathrm{Na}}$. $R_{m,j+1}$ is the $(j+1)$th zero of the Bessel function $J_m(\rho)$ (different from that at $\rho=0$ for $m\neq 0$), and ρ is the radial coordinate parallel to the surface. If the reflection at the island boundaries is not complete, one-electron energy-conserving transitions into substrate states are possible. The island-localized states turn then into resonances.

The calculated energies of the island localized states are presented in Fig. 1. The quantum number j of a given state is obtained from the nodal structure in the ρ dependence of the corresponding wave function. Starting from the 7 Na atom nanoisland two types of states clearly emerge forming the bands converging to −4.9 and −2.3 eV at $k_{m,j}=0$. The energies of these states closely follow the trend [Eq. (1)] predicted by the simple model of a particle in a cylindrical box. From the z dependence of their wave functions (see, e.g., Fig. 2) the states can be recognized as arising from the QWS and $n=1$ IS parent continua by quantization in the lateral direction because of the nanoisland boundary.

The QWS confinement at Na nanoislands has been studied earlier.[22] Here we are interested in the $n=1$ IS case. As follows from the present DFT study, the vacuum level of 1 ML Na/Cu(111) is located at −1.53 eV with respect to the vacuum level of Cu(111). Therefore the energies of the states originating from the $n=1$ IS confinement converge to −770 meV $(k_{m,j}=0)$ if measured with respect to the vacuum level of 1 ML Na/Cu(111). This is close to the value $E_{n=1}=-992$ meV at $\bar{\Gamma}$ reported above. At a first glance this result and a nice agreement with Eq. (1) might seem surpris-

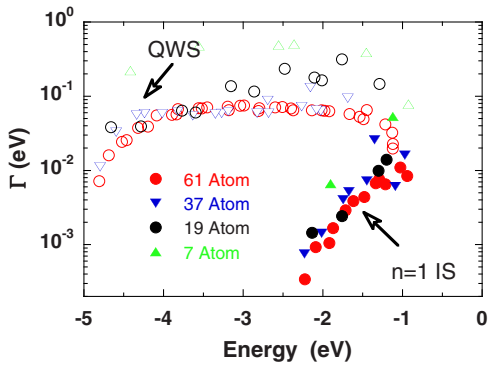

FIG. 3. (Color online) Widths of various (m,j) island-localized states as functions of their energy. Different symbols represent the states corresponding to the Na islands of different size, as shown in the inset. Open (closed) symbols give results for the states originating from the QWS ($n=1$ IS) localization.

ing. Indeed, the shift of the vacuum level for 1 ML Na/Cu(111) is due to the overlayer dipole formed because the work function of Na is lower than that of Cu. As for a finite size nanoisland, the dipole potential due to it vanishes at large distances so that the vacuum level is not affected. In order to understand present results, consider the spatial location of the $n=1$ IS electron. As follows from Fig. 2, the maximum of the electron density of the $n=1$ IS is located at $Z_{max}\approx 5$ a.u. from the surface of the Na nanoisland. Then, for sufficiently large islands with $R_{\mathrm{Na}}>Z_{max}$, the nanoisland induced potential as "seen" by the electron in the island-localized state does not differ from the potential of a complete Na monolayer. This observation explains the present results for the studied nanoisland sizes.

The electron-surface distance Z_{max} scales as n^2 with the principal quantum n of the ISs. One would then expect that the 61 Na atom island might allow for the confinement of the $n=2$ IS of the 1 ML Na/Cu(111) system. Indeed, we have found two $n=2$ states with $m=0$ symmetry and one with $m=1$ symmetry. We also could identify an $m=0$ state corresponding to the $n=3$ island-localized IS [$Z_{max}\approx 50$ a.u. for 1 ML Na/Cu(111)]. The calculated electronic densities of these states are shown in Fig. 2. Observe that the energies of the $n=2$ and 3 states are above the vacuum level of the 1 ML Na/Cu(111). This indicates that the nanoisland size is still not large for these high-n states and the finite size effects in the z direction are important.

We show in Fig. 3 the widths of island-localized states. For the given band of states (IS or QWS) the width decreases with decreasing $k_{m,j}$ [increasing binding energy, cf. Eq. (1)]. The energy dependence of the width is more pronounced than the dependence upon the island size. This finding is in line with the previously reported results for nanostructure-confined states.[9,10,22,27] It can be explained by a large reflectivity of the island boundaries for electrons with low $k_{m,j}$. In comparison with those of the QWS, the widths of the ISs are overall an order of magnitude smaller. This difference is even larger for the $n=2$ IS as follows from the data in Fig. 2. With the width of a fraction of meV, the ISs appear as nearly stationary states within the one-electron picture. Thus while the lifetime of the QWS at small nanoislands is determined primarily by the one-electron decay,[22] the lifetime of the island-localized ISs should be determined by inelastic interactions with substrate electrons. The corresponding decay rates Γ_{ee} can be estimated from the decay rates of the ISs at the 1 ML Na/Cu(111) surface as calculated within the many-body approach developed by some of us.[13] We find Γ_{ee} to be within the range from 5 to 20 meV for the $n=1,2,3$ ISs.[28]

We attribute the long lifetimes of the island-localized ISs to two effects. (i) The localized $n=1$ and 2 ISs appear high in the projected band gap of Cu(111). Then, the electron transfer into the substrate should involve a large change of the momentum parallel to the surface. The decay of the island-localized states is then blocked, similarly to the stabilization of excited states of individual alkali-metal adatoms.[29,30] (ii) The energies of the localized $n=1$ and 2 ISs are below the IS continua of the Cu(111) surface, so that their decay into the latter states is impossible. This is in contrast with the case of the ISs localized at Ar islands on Cu(100),[18] where the efficient decay into the Cu(100) ISs with the same n leads to very short lifetimes. Along these lines, the increase of the width of the $n=3$ island-localized IS, as compared to that of the $n=2$ IS is attributed to both its position outside the projected band gap and to the opening of the decay channel into the $n=1$ IS of the Cu(111) surface. However, for larger island sizes the $n=3$ IS should lower in energy and should be stabilized similar to the $n=2$ IS.

In summary, we have shown that well-resolved series of the confined image potential states develop on metal-supported metallic nanoislands provided that the work function of the adsorbate is lower than that of the substrate. The states possess very long lifetimes against one-electron decay into the substrate so that they are basically stable within the one-electron picture. Thus while very small islands lead to the 2D localization of the substrate ISs by the attractive nanoisland potential,[31] for the larger nanoisland sizes the situation corresponds to the confinement of the ISs of the complete adsorbate overlayer(s) by the island boundaries. By "larger" one should understand nanoislands with characteristic sizes greater than the mean distance between the IS electron and the surface. The phenomena reported here are robust, general, and independent of the particular Na-nanoisland/Cu(111) system that has been studied. Besides the aforementioned work-function condition, the ISs localization requires only that the substrate possess a projected band gap along the surface normal.

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