Comment on "Phase Contribution of Image Potential on Empty Quantum Well States in Pb Islands on the Cu(111) Surface"

The Letter by Yang *et al.* [1] presents an experimental scanning tunneling spectroscopy (STS) study of unoccupied quantum well states (QWSs) in Pb islands grown on the Cu(111) surface. The departure from particle-in-a-box energy dispersion has been observed with decreasing energy spacing between QWSs for the energies above 3 eV with respect to the Fermi level (E_F). This is attributed to the image potential felt by an electron at the Pb-vacuum interface. It is proposed that the experiment probes the quasi-image potential states (ISs) of the Rydberg-like series converging to the vacuum level (E_V) at 4.6 eV above E_F. We show here that this interpretation is incorrect and offer an alternative explanation.

Two well-documented facts invalidate the discussion presented in the Letter: (i) The work function of 4.6 eV used by the authors substantially differs from the values of up to 4.2 eV obtained in photoemission experiments and *ab initio* calculations [2,3]. (ii) For the bias of a few eV the tip-induced electric field in the junction overrides the image potential. The ISs at surfaces experience a Stark energy shift, and evolve into field emission resonances (FERs) [4–6]. Thus, the description of the metal-vacuum interface with image potential only is incorrect. We further illustrate [Fig. 1(a)] point (ii) with calculation of the energies of QWSs in free-electron Pb/Cu(111) as a function of a uniform electric field within a 1D model [7]. The states ($E \lesssim 3$ eV) localized inside the Pb film are only mildly sensitive to the applied field. As to the QWSs with essential IS character close to E_V: the field as low as 0.05 eV/a_0 (corresponding to the tip surface distance as large as 42 Å for the bias of 4 eV) destroys the Rydberg-like series in full accord with *ab initio* results [4].

Here we conjecture that the Pb band structure along the Γ–L direction perpendicular to the surface of the film is at the origin of the results reported in [1]. Conclusive evidence supporting our explanation is achieved with data analysis as developed in Ref. [8]. Within the phase accumulation model, QWSs induced by the Pb overlayer of thickness D at $\bar{\Gamma}$ are characterized by the phase relation $\phi(E_n) + 2D\mathrm{k}(E_n) = 2\pi n$. $\phi(E_n)$ is the scattering phase shift accumulated at the interfaces of the overlayer. If, for the overlayers D and D' there is a corresponding pair of quantum numbers n and n' such that $E_n \simeq E_{n'} = E$, the ϕ can be approximately canceled out, and the energy-dependent wave vector is $k(E) = \pi(n' - n)/(D' - D)$. Under the assumption that $E_n = E_{n'}$ for the states within 40 meV energy window (Δ), we obtain from the data of Ref. [1] the Pb band along Γ–L. Results are shown in Fig. 1(b) together with data from [8] for Pb/Ag(111) ($\Delta = 20$ meV) and *ab initio* band structure calculations [9]. The calculated band dispersion saturates at 5.4 eV for wave vector k approaching the reciprocal lattice vector $G = 1.161a_0^{-1}$, i.e., at Γ point. The agreement between the *ab initio* results, photoemission data [10], and these extracted from experimental STS data confirms the validity of our interpretation.

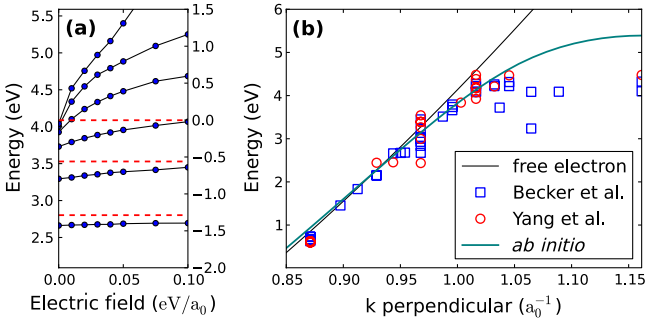

FIG. 1 (color online). (a) Calculated QWS energies (lines with dots) for 14ML-Pb/Cu(111) as a function of the electric field in the STM junction. The left (right) axis: the energy with respect to the E_F (E_V). Dashed horizontal lines: experimental data of [1]. (b) Bulk Pb band dispersion along Γ–L derived from experimental QWS energies (with respect to E_F). Results are compared with free-electron dispersion from the present 1D model and with *ab initio* calculations [9] (shifted by +0.4 eV to coincide with photoemission data in [10]).

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A. Zugarramurdi,[1,2] N. Zabala,[1,2]
A. G. Borisov,[3] and E. V. Chulkov[2,4]
[1]Elektrizitatea eta Elektronika,
FCT-ZTF, UPV/EHU, 48080, Bilbao, Spain
[2]CFM, Centro Mixto CSIC-UPV/EHU and DIPC, 20018, San Sebastián, Spain
[3]ISMO, UMR 8214 CNRS-Université Paris-Sud,
91405 Orsay CEDEX, France
[4]Física de Materiales,
UPV/EHU, 20080, San Sebastián, Spain

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