Quantum Well Behavior without Confining Barrier Observed via Dynamically Screened Photon Field

S. R. Barman,[1,2] P. Häberle,[3] K. Horn,[1] J. A. Maytorena,[4,5] and A. Liebsch[5]

[1]*Fritz-Haber Institut der Max-Planck Gesellschaft, 14195 Berlin, Germany*
[2]*Inter University Consortium, Khandwa Road, Indore, 452001, M.P., India*
[3]*Universidad Técnica Federico Santa María, Casilla 110-V, Valparaíso, Chile*
[4]*Centro de Ciencias Físicas, Universidad Nacional Autónoma de México, 62210 Cuernavaca, México*
[5]*Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany*
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Angle-resolved photoemission spectra from Na adlayers on Al(111) reveal features which behave like quantum well resonances although the substrate provides no confining barrier. These features are observed in a narrow photon energy range where overlayer collective excitations cause resonant enhancement of the photoemission intensity. The quantum well behavior is shown to be due to surface resonances of the Na/Al system. The resonances are observable using photoemission because of spatial confinement and dynamical enhancement of the local electric field within the Na films.

Quantum well states are a striking manifestation of elementary quantum mechanics. An electron confined in a one-dimensional potential well may occupy discrete energy levels whose quantum number *n* specifies the number of half-wavelengths spanning the well. Quantum well states have been observed experimentally in a variety of layered semiconductor and metallic films where potential barriers restrict the electron's motion in the direction normal to the film. They provide a conceptually simple means for studying electron confinement, but are also interesting for applications, e.g., in the giant magnetoresistance effect [1]. Angle-resolved photoemission is an ideal tool for studying the dependence of quantum well states on film thickness and on substrate and overlayer band structure [2–8]. Generally, the confining potential consists of the vacuum barrier, and a reflecting barrier due to a gap in the substrate band structure on the opposite side. The quantum states can thus be readily understood in terms of the discrete level structure of a one-dimensional potential well.

Here we discuss a different mechanism, namely, *quantum well behavior in the absence of a confining wall* between adsorbed metal film and substrate. The resonances are observable since the screened photon field is *dynamically enhanced and spatially confined* to the overlayer. While the former mechanism had been invoked earlier by Lindgren and Walldén [9] to explain spectral features observed in inverse photoemission from a Na monolayer on Al(111) [10], the special role of the photon field distinguishes the present system from ordinary quantum wells. We demonstrate that angle-resolved photoemission for Na on Al(111) in a wide range of coverages reveals quantum well-like spectral features associated with virtual states induced by the large *negative potential step* between overlayer and substrate. To observe these resonances it is crucial to suppress emission from substrate bands in the same energy region. This is achieved by tuning the photon energy to the collective modes of the overlayer. The local electric field is then enhanced and confined to the overlayer so that the Na resonances can be observed. Thus, while in usual quantum well systems the photon field plays no special role, here it serves as a novel mechanism ensuring the confinement of the excitation region.

The measurements were carried out at the 1 meter Seya-Namioka beam line at the Berlin BESSY-I storage ring using a commercial angle-resolved electron spectrometer at a base pressure of 6×10^{-11} mbar. *P*-polarized light was incident at 45°, and energy and angle resolution were about 150 meV and 3°, respectively. Na deposition was done at a substrate temperature of 100 K. One monolayer (ML) is defined as a close-packed Na layer. Coverage calibration and other experimental details were discussed previously [11]. A $(4/3 \times 4/3)$ low energy electron diffraction pattern was observed between 0.5 and 1 ML [12] beyond which a sharp *hexagonal* (1×1) pattern, indicative of epitaxial fcc Na layer growth, was observed.

The resonances observed in photoemission spectra for Na films on Al(111) are shown in Fig. 1 for increasing coverages. The clean Al spectrum, which is only 1 eV wide for 5.5 eV photon energy, does not reveal any features. Upon deposition of Na the work function decreases to 3 eV, making a wider range of binding energies accessible. A triangular feature (*A*) appears at a thickness of 1.5 ML. At 4.5 ML two new features appear at −0.8 eV (*B*) and −1.8 eV (*F*). At 7.5 ML peak *B* shifts to −0.4 eV, while feature *A* is absent. At about 15 ML, feature *C* appears at about −0.5 eV and moves up systematically until it reaches the Fermi level E_F near 33 ML. Features *D* and *E* which appear beyond 20 ML exhibit a similar behavior as a function of coverage. Peak *F* remains approximately stationary; its binding energy decreases only about 0.2 eV in the range between 5 and 50 ML. As will be discussed below, this peak is due to a direct interband transition within the Na layer. Thus, we find that with increasing overlayer thickness, spectral features within −1 eV
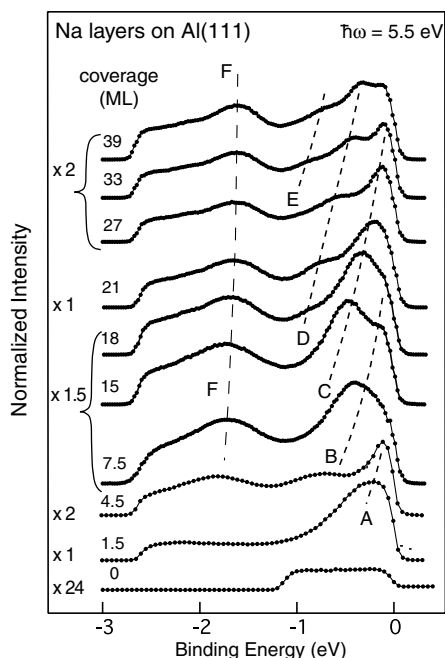
FIG. 1.   Photoemission spectra for various Na coverages on Al (5.5 eV photon energy, normal emission, $E_F = 0$). The intensity at E_F is normalized to unity. The actual intensities are given by the scaling factors on the right. Peaks ascribed to quantum well behavior are marked by letters A to E. Peak F is due to a direct interband transition in the Na layer.

binding energy disperse towards E_F. This behavior is strikingly similar to that of quantum well states with $k_\perp$ discretization. The parabolic dispersion with parallel wave vector (not shown) also suggests that the features originate from quantum well-like states. As shown in Fig. 2, the features do not disperse with photon energy, which rules out the possibility that they are due to direct transitions. The variation with coverage also indicates that they are not associated with surface states.
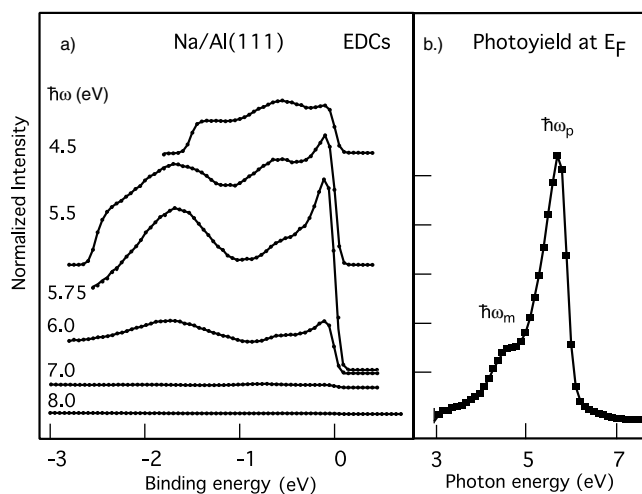

FIG. 2.   (a) Photoemission spectra for 5 ML Na/Al(111) for several photon energies (normal emission). The spectra are normalized to the incident flux. (b) Intensity at the Fermi energy as a function of photon energy.

Quantum well states for Na films on Cu(111) were observed previously. Electron confinement at the Na/Cu interface is provided by the Cu sp band gap at the L point [2]. On Al(111) this mechanism is absent since the narrow band gap at L lies about 1 eV below the Na valence band. Weak quantum well behavior was observed on Ag/Ni(111) [13] where the lattice mismatch is 14%. The occurrence of a reflection barrier was explained in terms of the loss of translational symmetry at the interface. Since Na/Al(111) has a lattice mismatch of only 4%, the resonance behavior is not likely to be associated with this mechanism.

The variation with photon energy shown in Fig. 2 has not been observed before and suggests a different mechanism as the origin of the resonances on Na/Al(111). Evidently, the observed quantum well behavior on Na/Al is intimately related to the dynamical screening properties of this system and to the frequency characteristics of the effective photon field. Whereas unscaled spectra for $\hbar\omega > 8$ eV are barely visible, an enormous enhancement is observed below 7 eV, with a maximum at 5.75 eV. Although the entire spectrum becomes intense, the enhancement is largest near E_F. The maximum corresponds to the frequency of the bulklike overlayer plasmon near $\hbar\omega_p$, with a shoulder close to the Na multipole surface plasmon at $\hbar\omega_m \approx 4.6$ eV [14,15]. This behavior differs fundamentally from that of ordinary quantum well states whose intensities follow that of bulklike interband transitions [16].

We thus explore the one-electron scattering processes giving rise to the quantum well-like behavior of the Na valence states *and* the influence of dynamical screening on the local electric field. For simplicity, we represent overlayer and substrate in terms of the jellium model [17] which, combined with the time dependent local density approximation [18], provides an excellent description of excitation spectra of adsorbed alkali metal films [11,15,19]. Figure 3 illustrates the ground state potential and the dynamical local potential, which includes the response of the electron density to the incident photon field. The potential step between Na and Al corresponds to the difference between their Fermi energies. Since the Al substrate does not provide a suitable band gap which can act as a reflecting potential barrier, the electronic states within the overlayer are continuous functions of energy and film thickness. In the region of constant Na potential the ground state wave functions may be written as $\psi_{k_\perp}(z) = A_{k_\perp} \sin(k_\perp z - \gamma_{k_\perp})$, where the normal momentum $k_\perp$ is measured with respect to the bottom of the Na potential and $\gamma_{k_\perp}$ is a boundary phase shift. z is the coordinate normal to the surface. The quasidiscrete nature of the Na valence band induced by the potential step at the Na/Al interface manifests itself in the oscillatory behavior of $A_{k_\perp}$ as shown in Fig. 4. Since $\gamma_{k_\perp}$ is slowly varying, the maxima of $A_{k_\perp}$ are approximately given by the condition $k_\perp a = n\pi$, where a is the overlayer thickness. Thus, below k_F there are about $n = k_F a/\pi$ peaks whose width results from single-particle hybridization with substrate states and depends on the thickness a and the potential difference between overlayer
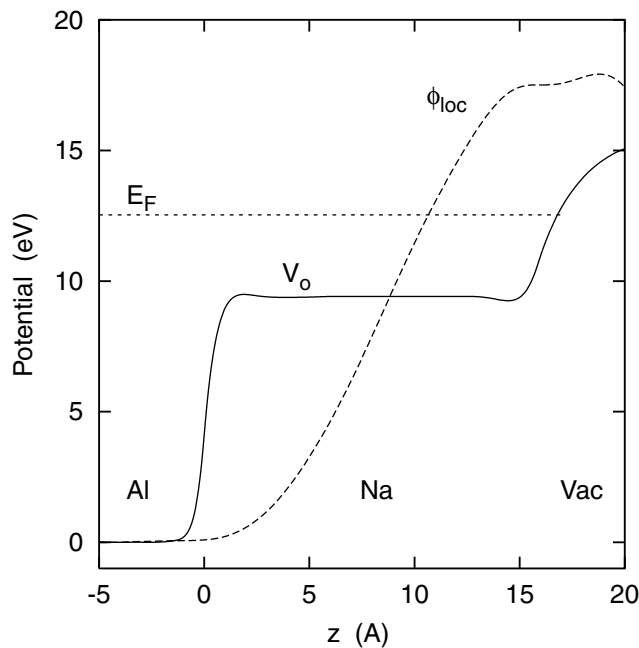
FIG. 3.   Ground state one-electron potential $V_0(z)$ (solid curve) and real part of dynamical local potential $\phi_{loc}(z, 5.5\text{ eV})$ (arbitrary units; dashed curve) for 5 ML Na on Al ($a = 16$ Å). E_F denotes the Fermi level.

and substrate. With increasing thickness the peaks become sharper and move to lower $k_\perp$ corresponding to higher binding energies. Apart from the broadening, therefore, the potential drop between Na and Al ensures that the overlayer resonances obey the same variation with binding energy and overlayer thickness as true quantum well states.
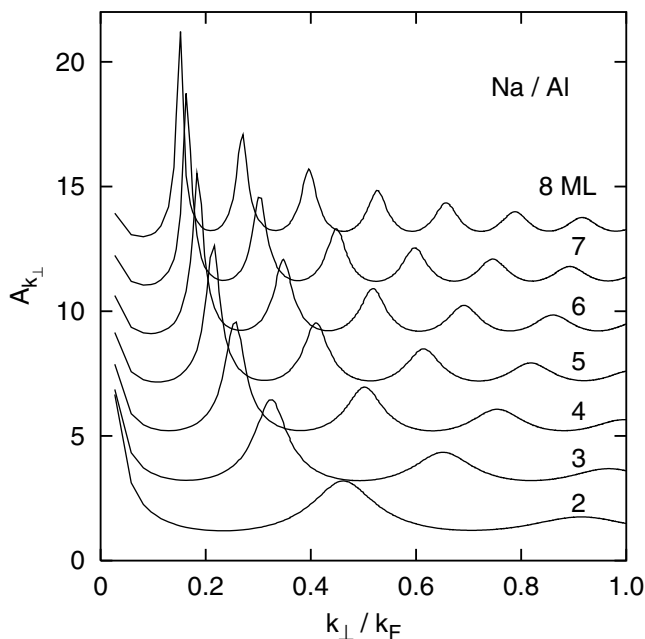
We now discuss the effect of the photon field which has a unique influence on the observed quantum well behavior. The screening response of the Na valence electrons to the incident photons generates an induced field normal to the surface which together with the bare photon field forms the effective local field governing the photoexcitation cross section. Our microscopic dynamical calculations show that this response becomes resonant near the overlayer collective excitations: the bulklike mode at $\hbar\omega_p$, whose fluctuating charge is a standing wave extending across the Na film, and the multipole surface mode at $\hbar\omega_m$, whose charge is concentrated near the Na/vacuum interface. Since the frequencies of these excitations are far below the Al bulk plasma frequency, the effective local field is spatially confined to the overlayer so that emission from substrate states is suppressed. This is illustrated in Fig. 3, which also depicts the dynamical potential ϕ_{loc}. Near $\hbar\omega_p$ the normal component of the local electric field in the overlayer, i.e., the gradient of ϕ_{loc}, is about 2 orders of magnitude larger than in the substrate.

As shown in Fig. 5, the quasidiscrete nature of the Na overlayer states leads to characteristic features in the photoemission spectra. Since the local potential limits emission to the overlayer, the matrix element for normal emission is proportional to the amplitude $A_{k_\perp}$ of the ground state wave function within the overlayer. Accordingly, the theoretical spectra exhibit a series of peaks which appear to move upwards as the overlayer thickness increases. At larger coverages, this pattern continues to evolve in a regular manner, with spectral peaks becoming more densely spaced, in close analogy to the experimental features

FIG. 4.   Amplitude $A_{k_\perp}$ of ground state wave function within Na overlayer as a function of $k_\perp$ for various coverages ($k_F = 0.9$ Å^{-1}). The maxima correspond to surface resonances induced by the potential step at the Na/Al interface.
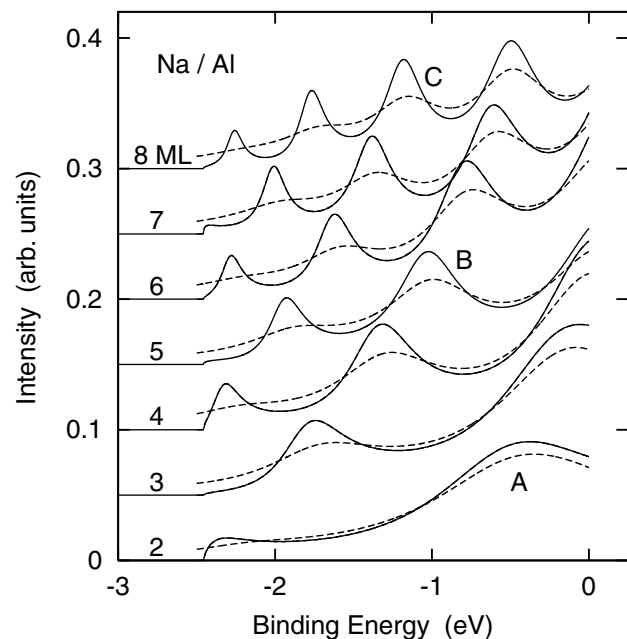

FIG. 5.   Calculated energy distributions for Na on Al for various coverages at 5.5 eV photon energy. The lower cutoff is due to the work function. Letters refer to analogous spectral features observed in Fig. 1. Dashed curves indicate the broadening due to hole lifetime and experimental resolution.

shown in Fig. 1. In practice, the oscillatory behavior of $A_{k_\perp}$ can be seen most clearly near E_F since various broadening mechanisms affect the deeper lying spectral features. To account for the hole lifetime we have included an imaginary self-energy of the form $0.1E_i^2$ eV, corresponding to the quasiparticle broadening of a homogeneous electron gas with electron density of Na [20,21]. In addition, we have accounted for the experimental resolution of 0.15 eV. At the coverages shown, the finite lifetime of the outgoing electron plays only a minor role since the mean free path is long compared to the overlayer thickness. Deviations from layer-by-layer growth, however, should give rise to peak averaging, in particular, at high binding energies. For these reasons, only quasidiscrete Na states within about 1 eV of E_F can be identified in the measured spectra.

We point out that the spectral peaks in the electron distribution curves actually move *down* with increasing coverage, despite the apparent upward shifts seen in Figs. 1 and 5. This contradiction may be readily resolved by analyzing how these peaks behave if plotted versus initial state momentum (see Fig. 4). As the coverage increases, more virtual states fit into the range between 0 and k_F. Thus, spectral peaks shift towards higher binding energies. The labels in Figs. 1 and 5 therefore merely serve to identify analogous experimental and theoretical spectral features.

The bulklike interband transition within the Na film can be qualitatively included via a one-dimensional pseudopotential. Since this potential is weak, the oscillatory behavior of the amplitude $A_{k_\perp}$ is preserved. The main effect of this potential is to add Fourier components to the final state related to the interplanar spacing. Remarkably, the energy of this direct transition (-1.5 eV binding energy at 5.5 eV photon energy) agrees with the data if the reciprocal lattice vector corresponds to (111) planes of an equivalent fcc lattice rather than to (110) planes of bulk Na. Since the overlayers exhibit a hexagonal electron diffraction pattern, these results support the epitaxial fcc-like growth up to rather large coverages. The variation of the fcc-like interband peak with photon energy is also in agreement with the data. The theoretical spectra indicate that the interband transition peak shows a Fano profile resulting from the interference of the discrete direct transition with the continuum of nondirect transitions from Na valence states. With decreasing overlayer thickness, this interference becomes stronger, giving rise to a broader, less symmetric line shape and a slight shift which is also seen in the data. The interband transition and its interference with the quantum well-like surface resonances of Na/Al will be discussed in a more detailed publication [22].

In summary, quantum well behavior was observed in photoemission from thin alkali metal films in the absence of a reflecting barrier in the band structure of the underlying substrate. Instead, the large negative potential step between overlayer and substrate gives rise to quasidiscrete levels within the overlayer that exhibit similar characteristics as traditional quantum well states. By tuning the photon frequency to the collective overlayer modes, emission from these levels is resonantly enhanced while emission from substrate bands is suppressed. Similar effects should be observable on other systems with large one-electron potential steps and well-separated collective excitations.

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