Probing Interface Electronic Structure with Overlayer Quantum-Well Resonances: Al/Si(111)

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The dispersion of quantum-well resonances in ultrathin epitaxial Al films on Si(111) reveals energy- and wave vector-dependent reflection properties at the Al/Si interface. The substrate electronic structure strongly influences the phase shift of the electron waves upon reflection at the interface. Thus the details of the substrate electronic structure need to be taken into account for a complete analysis of metallic quantum-well resonances. Furthermore, the assumption of loss of parallel wave vector information upon reflection or transmission through a lattice-mismatched interface is challenged. The changes induced in the electronic structure of the overlayer can be used to probe the ground-state substrate band edges.

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Confinement of electrons often leads to strongly modified physical properties. In a thin metal film electrons can be confined by an energy band gap or by a symmetry- or wave vector-dependent gap in the substrate on the one side, and the vacuum barrier on the other, leading to the formation of discrete quantum-well states that can be probed directly by angle-resolved photoemission [1–6]. Quantum-well states are not only interesting from a fundamental point of view, but can result in macroscopic effects as in the case of thickness-dependent oscillatory coupling between two ferromagnetic layers separated by a nonmagnetic spacer [7]. Most studies of quantum-well phenomena in thin metal films have so far concentrated on metal-on-metal systems [1,4–6], mostly involving noble metals. On the other hand, thin metal films on semiconductors may be the basis for novel devices utilizing quantum-well states.

It has been shown recently that, under an appropriate choice of growth parameters, epitaxial films with an abrupt interface can be prepared even for a reactive system such as Al/Si [8]. Here, the electronic and atomic structure of the interface is of great relevance, since it determines the growth mode of thin films, and the nature and even the existence of quantum-well states. Furthermore, to what extent electron momentum is conserved upon crossing an interface, still a subject of debate, is an important issue regarding the realization of metal-semiconductor spin filters [9] and the interpretation of ballistic-electron emission microscopy experiments [10]. Most surface science techniques, however, are not sensitive to the electronic structure of an interface buried many atomic layers below the surface. Here we demonstrate how, by analyzing details of the dispersion behavior of quantum-well states in Al layers on Si(111), the influence of the substrate band structure on the phase shift and reflectivity of Al valence electron waves at the interface in this *lattice-mismatched* system can be studied.

The experimental setup involves angle-resolved photoemission using synchrotron radiation from the 1m-Seya-Namioka monochromator at BESSY I (Berlin), incident on the sample at 45° [8]. Energy distribution curves were recorded with a commercial photoelectron spectrometer (ADES400), with an overall experimental resolution of $\approx$100 meV. Spectra were normalized to the photon flux, recorded simultaneously with each spectrum. The p-type Si sample was cleaned by resistive heating, and Al was evaporated from a Knudsen cell at rates of $\approx$1 Å/min while the substrate was maintained at $\approx$100 K via a liquid nitrogen cold finger. The base pressure in the vacuum chamber was 7×10^{-11} mbar ($\leq 3 \times 10^{-10}$ mbar during Al evaporation). Deposition of Al on Si(111) at 100 K induces an abrupt and homogeneous interface and leads to the growth of an epitaxial, two-dimensional Al(111) overlayer of good crystalline quality as evidenced by the sharp low-energy electron diffraction pattern. Even after annealing to room temperature and above, the films are highly stable and improve their crystalline order while retaining their 2D character, and the interface remains homogeneous, in contrast to films grown directly at room temperature [8].

The high quality of films deposited at low temperature permits the observation of quantum-well resonances in the as-deposited films for thickness up to 30 Al monolayers (1 ML = 2.34 Å), as can be seen in Fig. 1; the peak at highest binding energy is the Al(111) surface state [11]. The normal emission spectra exhibit well-defined separate peaks in the quasifree electron s-p band region, in increasing numbers with overlayer thickness. These photoemission peaks correspond to the discrete set of the normal component of electron wave vector $k_\perp$ allowed for each thickness as shown schematically in the inset, and can be readily understood within the phase accumulation model [12,13]. Here the metallic film is considered as a 1D potential well in the direction normal to the surface, where the quasifree valence electrons are confined between vacuum and substrate. Only those $k_\perp$ values fulfilling the stationary state condition $2kd + \Phi_B + \Phi_C = 2\pi n$ are allowed, where n is an integer, the thickness is $d = Na$ (a = lattice constant, N = number of atomic layers), and

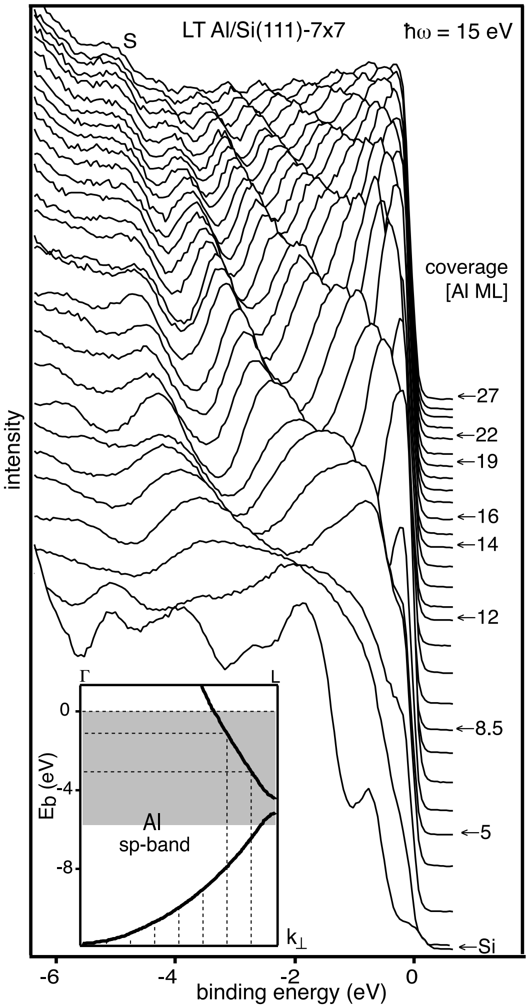

FIG. 1. Low temperature Al/Si(111) deposition series. The $\overline{\Gamma}$ Al(111) surface state, at the surface Brillouin zone center [11], is the deep-lying peak marked with an S, which reaches a binding energy of -4.68 ± 0.03 eV for thickness above its decay length of 12 ML [8]. The inset shows the s-p band of Al (the shaded region is the one measured experimentally) and schematically the allowed states for a 7 ML film.

Φ_C and Φ_B are the phase shifts at the metal/substrate interface and surface barrier, respectively. The phase shift upon reflection at the surface barrier (image potential) is well described by a semiempirical formula [14]. It is, however, not clear which phase shift should describe the reflection at the metal/substrate interface. Quantum-well states may decay into the substrate since silicon has several bands in the energy region investigated, and the interface is lattice mismatched. From the data in Fig. 1 it is obvious that, even without an energy gap, there is still a finite reflectivity at the Al/Si interface. Partial confinement of electrons in the metal overlayer results in so-called quantum-well resonances, which appear broader than quantum-well states in the photoemission spectra. In most quantum-well studies the Φ_C contribution is neglected, or, in case of lattice mismatch, a diffuse scattering condition with loss of all parallel wave vector information is assumed [15]. We show below, however, that the reflectivity and phase shift at the interface are largely determined by the substrate electronic structure and that they are energy and wave vector dependent.

Quantum-well features show no dispersion with photon energy, i.e., with $k_\perp$, due to their 2D character, but the dispersion parallel to the film $E(\mathbf{k}_\parallel)$ is unperturbed, since in this direction the overlayer has translational periodicity. For each overlayer, the dispersion of the quantum-well features in the surface Brillouin zone can be measured by changing the detection angle θ according to $k_\parallel = \sqrt{(2m/\hbar^2)E_{\text{kin}}}\sin\theta$. Such an in-plane dispersion series for a 23 ML Al/Si film is plotted in Fig. 2. The free-electron-like dispersion of the $\overline{\Gamma}$ surface state and up to six resonances can be followed, as well as the appearance of the surface resonance centered at $\overline{M}$ [11] for high angles. Both surface features are observed to cross, and the Al(111) $\overline{\Gamma}$ surface state becomes a resonance at high $k_\parallel$ values and disperses up to the Fermi energy E_F. The effective mass m^* for the in-plane dispersion of the $\overline{\Gamma}$ surface state and the quantum-well resonances is also indicated in Fig. 2, in units of m_e. The effective mass values agree to within a few percent with those predicted from self-consistent calculations [16], except for the leading quantum-well peak, where the experimental effective mass is 25% higher. The apparent deviation of m^* from theoretical predictions for states near E_F, which is larger for thinner films, is explained as an influence of the substrate band structure below.

In order to identify subtle energy shifts and intensity modulations of the photoemission features, we use an alternative graphic representation of the in-plane dispersion series: gray-scale images of the photoemission intensity (or its derivative) versus E_b and $k_\parallel$. Such band structure "maps" for three different Al/Si(111) films are shown in Fig. 3. The images represent the first derivative of the normalized intensities with respect to the binding energy,

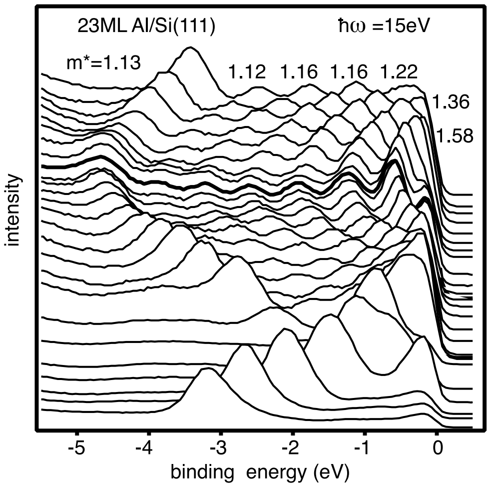

FIG. 2. Photoelectron spectra of an annealed 23 ML Al film for different detection angles, corresponding to $k_\parallel$ along $\overline{\Gamma M}$. The thicker trace corresponds to normal emission.

for 3(a) 3, 3(b) 7, and 3(c) 12 ML. They have been constructed from the experimental energy distribution curves collected for many different angles, interpolating the intermediate points. The data in 3(a) and 3(c) were recorded with 15 eV photon energy, in 3(b) with 13 eV. At first glance, the experimental dispersion can be well explained in terms of the Al band structure, and characterized by quasifree electron parabolas with effective masses close to m_e. However, a closer look reveals a modulation of the intensities in some regions, as well as slight shifts of the maxima with respect to the ideal parabolic dispersion, which cause the bottoms of the parabolas to appear flat (see Fig. 3c) or even folded towards lower binding energy (Fig. 3b, for example, at $E_b = -3.5$ eV near the zone center). The same features can be recognized in images constructed from the spectra without differentiation (not shown), albeit with a lower contrast. In order to highlight the modulations superimposed on the free-electron-like dispersion of the Al features, in the form of intensity depressions as well as shifts of the resonance maxima, an identical set of markers has been added to all three images, although not all modulations are recognizable in each of them. The markers follow the dark features which deviate from free-electron-like behavior (dark corresponding to steepest descent). The images have been constructed from the first derivative of the spectra in order to achieve enhanced contrast. The intensity modulations and the deviations from parabolic behavior appear strongest for the thinnest films. In Figs. 3b and 3c, the lower branches mark the region where the dispersion appears flat or "upside down."

The energy and intensity shifts observed in the $E(\mathbf{k}_\parallel)$ dispersion of the Al quantum-well resonances can be interpreted as a signature of the underlying Si substrate band structure as follows. Note that all modulations in the $E(\mathbf{k}_\parallel)$ diagram of Fig. 3, indicated by markers, have a downwards dispersion from the surface Brillouin zone center, as expected for a semiconductor whose bands have their minimum in binding energy there. Consider the results of a calculation of Si bulk bands projected onto the (111) surface along the $\overline{\Gamma M}$ direction in Fig. 3d, using density functional theory (DFT). The image represents the projected density of states, bright corresponding to areas of high density of states, largely coincident with the bulk band edges. There exists a clear correspondence between the bright areas in Fig. 3d and the set of markers obtained from the experimental data throughout a large part of the surface Brillouin zone. The markers are the same as those superimposed on the images (Figs. 3a–3c) and correspond to decreasing photoemission intensity. Thus, a high density of substrate states directly translates into lower interface reflectivity and less effective confinement. Notice in Fig. 3c how the contrast is higher in the region delimited by the lower branches of the marker set, in the region where Si presents no density of states. We conclude from the data that the phase shift due to reflection of the electron wave function at the interface is also affected: energy shifts of the quantum-well resonances are induced when they cross a substrate band edge (around 4 eV in Fig. 3b and 3.3 eV in Fig. 3c, for example).

For the valence electrons in the overlayer the substrate is not a "hard wall," nor is their phase shift upon reflection uniform with binding energy. Rather, the substrate has a distinct electronic structure consisting of several bands with different symmetries, and with band edges at specific points in $E(\mathbf{k})$ space which will strongly influence the reflection and phase shift properties of the electron waves at the interface. The modified reflection

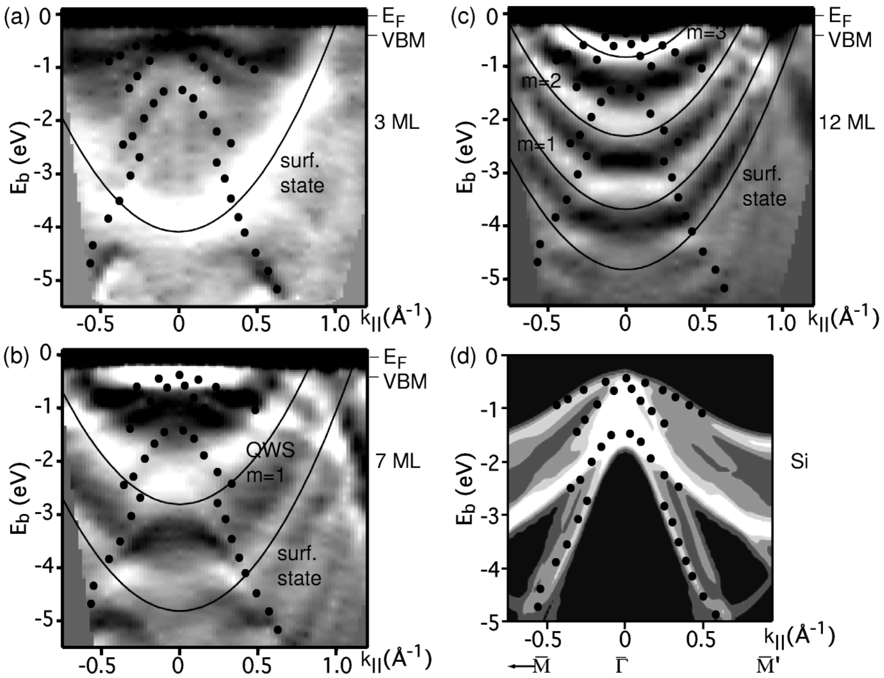

FIG. 3. (a)–(c) First derivative of the normalized intensities with respect to the energy for different Al/Si(111) films. The expected free-electron-like Al dispersion is indicated by black lines and the observed deviations from this behavior, i.e., the modulations of the Al features, have been summarized in a single set of black markers. (d) DFT local density approximation calculation Si bulk bands projection on the (111) surface. Bright areas represent high density of states.

properties result in a subtle modulation of the overlayer electronic structure, and need to be taken into account for a complete analysis of the dispersion of metallic quantum-well resonances. The effect appears weaker and eventually fades out for thicker films, as the phase shift at the interfaces becomes a smaller fraction of the round-trip phase accumulation:

$$k = \frac{n}{N}\frac{\pi}{a} - \frac{1}{N}\frac{\Phi_B + \Phi_C}{2a}, \tag{1}$$

where $n = N, N - 1, N - 2, \ldots$ for the quantum-well states considered, while $\Phi_B + \Phi_C \sim \pi$. The effect of the valence band maximum of silicon, above which the quantum-well states lie in an absolute band gap, is strongest in the spectra, as evident from the modulation within about 1 eV of E_F. It is still noticeable even through a 23 ML film, in that the dispersion of the shallowest quantum-well feature is flattened with respect to the free-electron dispersion (see Fig. 2). Mueller *et al.* [17] found that a maximum in Φ_B occurred at the energy position of the band edge of the substrate, and proposed this to be a general interface property. Here we show that a change in boundary conditions at the Al/Si interface affects the quantum-well resonances in their entire energy and wave vector range. A decrease in reflectivity and an abrupt change in the phase shift upon reflection at the interface, as a consequence of enhanced coupling of the overlayer resonances to substrate states, are detected at several band edges of the substrate, and not only at the border to an absolute energy gap, and they are followed throughout the surface Brillouin zone. The fact that the modulation features are not photon energy dependent confirms that the band edges are determined by observing the interference (quantum-well) effects on the Bloch electron wave between the two boundaries of the Al overlayer. The modulations are not caused by direct transitions between Si bands, which in any case would be obliterated for thicknesses of 7 ML and above (Figs. 3b and 3c).

Even though the escape depth of the photoexcited electron is rather short, an interface buried at a large depth below the surface can still be examined because the interference effect is inherently a ground-state property; the interface is actually probed by the valence Bloch electrons in the Al overlayer. The band edge determination does not suffer from the disadvantages of probing directly through an optical transition, such as the need to model or experimentally determine the final state bands. We note in passing that the Schottky barrier Φ_b^p may be directly evaluated from data such as in Fig. 3, since the separation between major band edges and the valence band maximum is precisely known ($\Phi_b^p = 0.50$ eV from Fig. 3); the valence band maximum and Fermi level are measured *simultaneously*.

The detailed substrate band structure has, until now, not been taken into account for the interpretation of quantum-well resonances spectra from ultrathin metallic overlayers. Our observations demonstrate that the effect of individual band edges can modify the overlayer electronic structure. Moreover, the substrate electronic structure becomes accessible to photoelectron spectroscopy. Our data clearly challenge the assumption that all parallel wave vector information is lost upon crossing an interface of a lattice-mismatched heterojunction, since we find modulations that are resolved in $\mathbf{k}_\parallel$. Recently, Dähne-Prietsch and Kalka [10] have also obtained evidence that the lateral momentum is conserved to a very high degree at the Au/Si(111) interface in their ballistic-electron emission microscopy experiments.

In summary, we find energy- and wave vector-dependent modulations of quantum-well resonances in epitaxial Al(111) films on Si(111), which reflect the band edges of the underlying Si bulk bands. A detailed understanding of interface electronic structure is found to be necessary for a full description of quantum-well resonances. This observation may be useful for probing ground-state substrate band edges in a variety of interface systems.

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