Shifts and widths of metal-overlayer quantum-well states near E_F observed by photoemission

A. Carlsson, S.-Å. Lindgren, C. Svensson, and L. Walldén

Physics Department, Chalmers University of Technology, 41296 Göteborg, Sweden

(Received 29 July 1994)

Photoelectron energy spectra reveal discrete valence-electron states in the range 0–220 meV above E_F for 1–3 atomic layers of Na on Cu(111). Apart from a stepwise dependence on the number of atomic Na layers the energy of the quantum-well states depends in a gradual manner on how full the layer is. The states are as well defined in energy as comparable surface states producing peak widths (50–90 meV), which depend on temperature and coverage.

Electron- as well as phonon-quantum-well-type states may be observed for metal films on metal substrates for overlayer thicknesses down to a monolayer.[1,2] In the case of electrons one may even include the submonolayer coverage range, where metal adsorbates can shift the energy of substrate surface states considerably and in a gradual manner when the submonolayer coverage is changed.[3] The discrete overlayer quantum-well states are formed by valence electrons, which are confined to the adsorbed film due to the existence of a substrate band gap in the energy range considered. There is no strict confinement since the state extends with an oscillating tail into the substrate and this tail may for a few atomic-layers-thick films and energies near the edge of a substrate band gap accommodate a large fraction of the electronic charge. In the ideal case of a homogeneous thickness the overlayer states will form a number of subbands, each with a well-defined energy for a given wave-vector component parallel to the surface. In the film the states have perpendicular wave vectors $k_\perp$ given by the phase-shift condition $\Phi_B + \Phi_C + 2k_\perp d = 2\pi m$, $m = 0,1,2, \ldots$, where d is the thickness. Φ_B and Φ_C are the phase shifts at the boundaries of the film towards the vacuum and substrate, respectively, and m is the quantum number characteristic of a subband. Via observation of these states, which has been made by tunneling and photoemission methods, information may be obtained about bulk-band dispersion,[4–7] phase shifts at buried interfaces,[5,8] substrate-induced spin polarization of overlayer states,[9–11] and the growth mode of thin-film overlayers.[12]

The purpose of the present paper is to show that, with the use of high-resolution photoemission ($\Delta E = 5$ meV), qualitatively different information may be obtained about metal-overlayer quantum-well states. Energy shifts and linewidth changes are observed when the coverage is changed and a temperature dependence is found for the linewidths. Previous work has given little information about how well defined in energy metal-quantum-well states are. For states near E_F, such as those discussed below for 1–3 atomic layers of Na on Cu(111), small shifts and changes of energy spread are essential for understanding properties involving low-energy excitations. One such property is the optical antiabsorption resonance observed in the infrared very recently for Cu(111)/Na and ascribed to electronic excitations of a charge-density-wave condensate at the Cu-Na interface.[13]

The present angle-resolved photoelectron-energy spectra are recorded with a high-resolution (5 meV) electron-energy analyzer (Leybold EL23) using a 1-mW He-Cd laser ($\lambda = 325.4$ nm) as light source. The sample is prepared by evaporation of Na from a heated glass ampoule broken in vacuum onto an electropolished Cu(111) crystal cleaned by Ar-ion sputtering and heating. While photoemission is usually employed to probe states below E_F, the present setup gives a sufficient intensity to observe quantum-well states for Na on Cu(111) in an energy range extending to around $10kT$ above the Fermi energy. To compensate for the reduced occupancy of states above E_F the energy distributions shown below are the recorded spectra multiplied by $1 + e^{(E - E_F)/kT}$. Prior to multiplication a flat spectrometer background intensity is subtracted from the spectra. This has an appreciable effect only near the high-energy limit of the probed range. The Fermi-Dirac factor is calculated using the experimentally determined position and width of the Fermi edge at small Na coverages or high emission angles when the photoelectron energy spectrum is rather flat below the Fermi edge.

Normalized to unit occupancy as described above, the spectra obtained for one, two, and three atomic layers of Na show well-defined emission peaks at initial-state energies 0.1 eV below E_F (1 ML) and 0.1 eV (2 ML) and 0.2 eV (3 ML) above E_F, respectively (Fig. 1). The intensity of the emission peaks is high. For the monolayer state 0.1 eV below E_F it is around 10^7 counts/sec with p-polarized light incident at an angle of 79°.

The energies of the states assigned to one and two atomic layers of Na are found to shift gradually with changing coverage (Figs. 2 and 3). The monolayer state has been observed previously[1,14,15] but the coverage dependence of its energy was not noted. A reason for this lack of observation is that the energy is normally difficult to measure by photoemission when it falls above the Fermi edge, which is the case for Na coverages less than 0.85 ML [Fig. 2(b)]. The energy of this state shifts downwards almost linearly with increasing monolayer amounts of Na on the surface until a certain coverage is reached, when the energy shifts at a much smaller rate upon further deposition. This occurs at an energy of 100 meV below E_F and the breakpoint probably marks the completion of the first atomic layer. This is supported also by the observation that the area under the peak decreases rapidly if the deposition is continued beyond this coverage. The height of
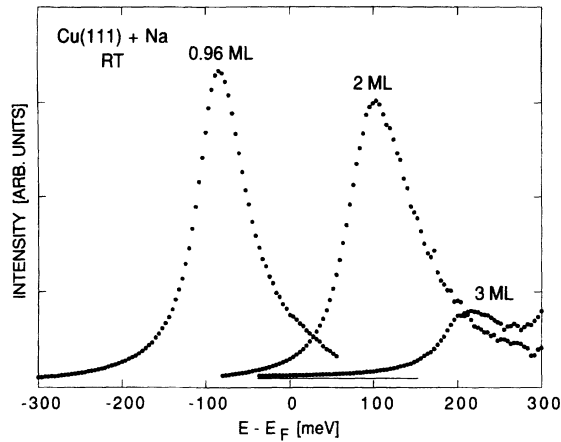
FIG. 1. Photoelectron energy spectra multiplied by $1 + e^{(E-E_F)/kT}$ recorded in the normal direction from Cu(111)/Na at Na coverages near 1-, 2-, and 3-ML Na and a photon energy of 3.82 eV. The light is p polarized and incident at an angle of 79°.

the peak, however, begins to decrease when the coverage exceeds 0.96 ML [Fig. 2(a)]. For coverages between 0.96 and 1 ML the reduced height is accompanied by a broadening of the emission peak [Fig. 2(a)]. For coverages between one and two atomic layers there appears one emission peak due to the monolayer-thick parts of the film and one due to the two-atomic-layers-thick parts (Fig. 3). The energy distributions shown in Fig. 3 were obtained with the sample holder cooled with liquid N_2 but similar spectra are obtained also when the sample is at RT. The main effect of cooling is that, as discussed below, the emission peaks become narrower. The evaporation time needed to produce maximum intensity of the 2-ML peak and saturation of the energy is close to twice the time needed to form the first full atomic layer. This indicates that the growth occurs in a nearly layer-by-atomic-layer fashion. The energy of the 2-ML state remains nearly constant until the coverage reaches 1.7 ML and then drops by around 30 meV between 1.7 and 2 ML (Fig. 3). The monolayer peak is clearly observed for coverages up to 1.75 ML and the energy is then around 25 meV higher than at 1 ML.

The peak due to the quantum-well state of the 3-ML-thick film (Fig. 1) has an appreciably lower intensity than the corresponding peaks recorded for the 1- and 2-ML-thick films. In previous work, based on the decay of substrate emission peaks as Na is deposited on a Cu(111) surface, it was concluded that at RT no more than three atomic layers can be grown in a layer-by-atomic-layer fashion.[16] From the low intensity of the 3-ML peak it would appear that even the third atomic layer is incomplete.

The states near E_F discussed here satisfy the phase condition $\Phi_B + \Phi_C + 2k_\perp d = 2\pi m$ for quantum numbers $m = N$, where N is the number of atomic layers and $d = Na$, a being the atomic-layer thickness. In this series could be included also, as the $m = N = 0$ case, the Cu(111) surface state 0.4 eV below E_F since this state has an oscillating tail in the substrate similar to the tails of the overlayer states. As the film becomes thicker the perpendicular wave vector $k_\perp = \pi/a - (\Phi_B + \Phi_C)/2Na$ approaches π/a. The observation of higher energies for higher values of N means that the sum of
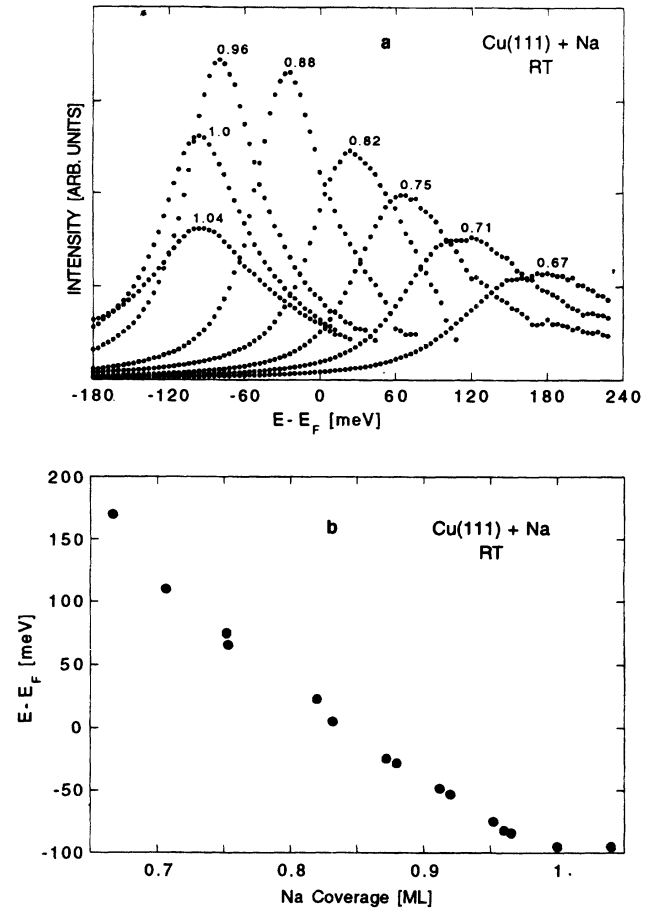

FIG. 2. (a) Photoelectron energy spectra multiplied by $1 + e^{(E-E_F)/kT}$ recorded at a photon energy of 3.82 eV in the normal direction to Cu(111) covered by different monolayer amounts of Na. The evaporation times in seconds are indicated in the diagram. A full Na monolayer is obtained after around 750 sec. The light is p polarized and incident at an angle of 79°. (b) Energy vs coverage for the state characteristic of 1 ML of Na on Cu(111).

the barrier phase shifts is a positive quantity near E_F. Assuming free-electron dispersion, one finds from the peak positions measured at RT ($E - E_F = -100$, 104, and 210 meV for 1, 2, and 3 ML of Na) that $\Phi_B + \Phi_C = \pi[0.17 + 0.2(E - E_F)]$ for energies around E_F if the separation from the Fermi energy is given in electron volts. From the measured energies one may estimate that the limiting energy of the $m = N$ series of states would be around 0.45 eV above. However, at RT no layer-by-layer growth is observed beyond the third atomic layer. The energies observed for the overlayer states are thus as expected and the main point of interest is that states as far above the Fermi level can be detected by photoemission.

Next we discuss the two features for quantum-well systems observed in the present experiment, namely, the gradual energy shifts with changing coverage and the linewidth changes obtained when temperature or coverage is changed. The large energy shift found for the 1-ML state and the small shift obtained for the 2-ML state are both, we believe, related to the growth mode of the film. In the monolayer coverage
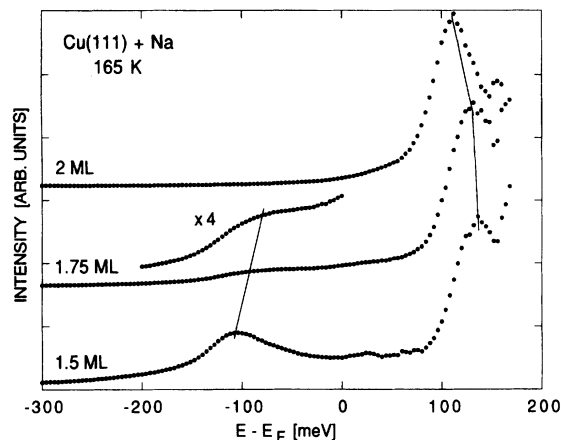
FIG. 3. Photoelectron energy spectra multiplied by $1 + e^{(E-E_F)/kt}$ recorded in the normal direction from Cu(111) covered by different amounts of Na between 1 and 2 full atomic layers. The light is p polarized and incident at an angle of 79°.

range there is, as for several alkali overlayer systems, a uniform adatom distribution with a well-defined nearest-neighbor distance, which decreases as more alkali metal is adsorbed.[17] The coverage dependence of the energy of the quantum-well state can be estimated by assuming that the monolayer defines a volume that is filled by an electron gas that becomes denser in proportion to the number of Na atoms in the layer. If one uses a simple phase model, which has turned out to produce surprisingly accurate energies for surface and thin-film states, the estimated energy shift is close to the measured one. For details of the model and its application to the present system the reader is referred to the literature.[18,19] The main reason for the downshift is that the potential well representing the monolayer becomes deeper as the adatom and electron-gas density in the overlayer increases. The monolayer state observed in spectra recorded along the surface normal is the low-energy edge of a parabolic band, which becomes increasingly occupied as the edge shifts to energies further below E_F. By changing the Na coverage the electron density in this band can therefore be varied over a wide range and from quite low values.

To explain the shift observed for the state characteristic of 2 ML of Na we note that the second layer grows via the formation of one-atomic-layer-thick islands on top of the first full atomic layer. This is demonstrated by the appearance for coverages between one and two atomic layers of two emission peaks, one of which is due to 1-ML-thick areas of the film and the other to 2-ML-thick areas (Fig. 3). A shift to lower energy of the 2-ML state when the coverage is increased can then be explained as a lateral quantum-size effect provided that the average island becomes larger as more Na is adsorbed. For an island regarded as a quantum dot, the smallest value for the lateral component of the wave vector will be approximately π/D, if D is the distance across the island. A rough estimate of the size dependence of the energy for a dot of free-electron metal is then given by $h^2\pi^2/mD^2$. Equating this with the 30-meV shift observed between 1, 7, and 2 ML gives an island size of around 50 Å.

When the sample is kept at RT the overlayer states produce photoemission peaks with a breadth [70–90 meV FWHM (full width at half maximum)] that is somewhat larger than observed for comparable surface states such as the Cu(111) (FWHM 70 meV) (Ref. 20) and Ag(111) (50 meV FWHM) (Ref. 21) surface states 0.4 and 0.1 eV below E_F, respectively. Low-temperature data, available for Cu(111),[20,22] show that the width of the surface-state emission peak is little affected by cooling. By contrast, the widths of the overlayer-state peaks become smaller when the temperature is reduced. As the temperature is reduced from $kT = 25.7$ to 14.5 meV the width of the monolayer-state peak decreases from 72 to 50 meV. For the duolayer state the corresponding breadths are 75 and 48 meV. The width of the monolayer state is then measured at a coverage slightly lower than 1 ML. Apart from the larger thermal broadening at RT, due to the low Debye temperature of Na, the energies of the quantum-well states in the thin metal overlayers are thus as well defined as the surface-state energies measured for clean noble metals.

As discussed previously for surface states,[23] photoemission peak widths are larger than may be explained by the electron-electron scattering and the experimental resolution. It was suggested that phonon emission during the photoemission process is responsible for the enhanced width. This mechanism is expected to be only weakly dependent on temperature and is therefore not likely to explain the present results. In the present case an energy spread is expected due to the film-thickness modulations produced by the longitudinal-acoustic, organ-pipe-like phonon modes observed recently for 2–20 ML of Na on Cu(100).[2] These have a node at the first substrate layer and a maximum at the surface. For a 2-ML-thick film the phonon energy is around 8 meV. For 1 ML the corresponding energy is 17.8 meV. The lower frequency for the 2-ML film means that the amplitude is larger making the relative thickness modulations rather similar for 1- and 2-ML-thick overlayers. This may explain why the experimental widths are similar for the two thicknesses.

In addition to the temperature dependence discussed above, the widths of the emission peaks also depend on the alkali-metal coverage. This dependence is particularly strong in a small coverage range near completion of the first atomic layer when, between 0.96 and 1 ML, the peak due to the monolayer state changes its width from 72 to 105 meV at RT (Fig. 2). The reason why the quantum well becomes less well defined in this coverage range could be that there are atoms residing in the second atomic layer already when the first atomic layer is still incompletely filled. Regarding the monolayer-state peak, we furthermore note that it is wider at low coverages, when the adatom distribution is uniform but disordered, than at high monolayer coverages, when the low-energy electron-diffraction (LEED) pattern shows that the Na atoms form a hexagonal overlayer. A recent, detailed LEED investigation[17] showed that the formation of an ordered pattern occurs in the coverage range between 0.8 and 0.9 ML. The present observation of a narrow emission peak between 0.85 and 0.96 ML thus indicates that the width is closely related to the degree of atomic order.

Our final comment concerns the antiabsorption resonance recently observed for the Cu(111)/Na system.[13] When this

optical measurement is compared with the present results there is a striking contrast between the shifting energies for the states characteristic of the system and the nearly constant energy observed for the antiresonance when the Na coverage is varied. One may therefore conclude that the antiresonance is not related in a simple manner to the electronic level structure observed here.

In summary we have used photoemission to probe thermally populated states with energies reaching $10kT$ above E_F. Quantum-well-type states for Na overlayers on Cu(111) have energies that are as well defined as the energies of comparable surface states. It is suggested that standing-wave-type vibrational states give an important contribution to the temperature dependence of the photoemission peak

width. This width furthermore depends on the coverage in a way that shows that disorder gives an important contribution to the width. The energy of the monolayer state depends on coverage in a way that can be understood by regarding the monolayer as a slab of electron gas, which becomes denser when the alkali-metal coverage increases. A small coverage dependence observed for the energy of the quantum-well state characteristic of two atomic layers is ascribed to the growth of the second layer via the formation of islands with a quantized lateral motion for the valence electrons.

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