Layer-by-atomic-layer desorption of Cs from Cu(111)/Cs observed via photoemission

LETTER TO THE EDITOR

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S Å Lindgren and L Walldén

Physics Department, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Abstract. For Cs on Cu(111) the work function is found to depend on the Cs thickness for coverages less than three atomic layers. The magnitude of the work function variation is as predicted for a free-electron-like quantum well. The photo-yield observed for a photon energy slightly above the threshold for photoemission can be used as a measure of the adsorbed amount. Via the yield, the thermal desorption of the first three atomic layers can be followed layer-by-atomic-layer. The desorption energy differs by around 35 meV between the second and third layer.

In an adsorbed metal film one may find discrete states formed by valence electrons that have energies and parallel wave vectors within a substrate band gap. Effectively, for these electrons, which propagate forever back and forth between the vacuum barrier and the adsorbate/substrate interface, the overlayer can be regarded as a quantum well. Overlayer states of this type were first observed by tunnelling spectroscopy for metal films thicker than about 150 Å deposited on an insulator [1]. Later work has shown that with a metal substrate these states can be observed for thicknesses down to one monolayer, a range where quantum size effects should be more dramatic [2].

Apart from the possibility of finding properties that are different from those of conventional samples, the quantum well systems provide us with an opportunity to obtain unique information about the overlayer metal and solid/solid interfaces [1–5]. In the present article we report on the observation that the work function depends on the overlayer thickness for Cs adsorbed on Cu(111) and that the photo-current measured for a photon energy slightly higher than the threshold for photoemission can be used as a measure of the adsorbed amount, making it possible to study the thermal desorption of the adsorbate layer-by-atomic-layer. We concentrate on the results obtained for multilayers. The properties of alkali monolayers have been discussed extensively in previous work [6].

For adsorbed alkalis the usual result is that $e\Phi$ saturates at around full monolayer coverage [7, 8]. For Cs on Cu(111) we find that the work function shows an easily measured thickness dependence for the first three atomic layers. Samples were prepared by Cs evaporation onto the Cu(111) substrate from a heated ampoule broken *in situ*. To ensure adsorption of more than around 90% of one full atomic layer, which is the saturation coverage at room temperature, and allow the adsorbate to order, the sample is kept at around 200 K during the Cs deposition. The thickness is obtained from the evaporation time, using as the reference the time needed to form one full atomic layer.
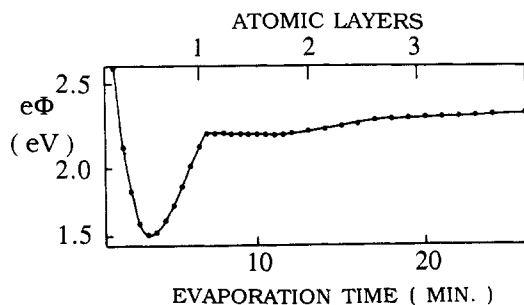
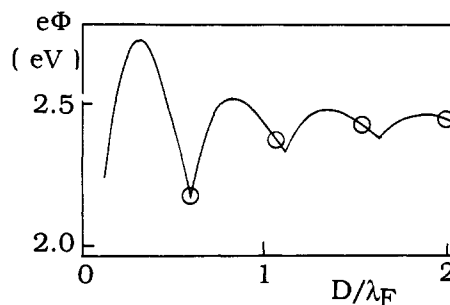**Figure 1.** Coverage dependence of the work function for Cs on Cu(111).

Figure 2. Thickness dependence of the work function for a thin film of jellium with $r_s = 6$ as calculated by Schulte [8]. D is the thickness and λ_F is the Fermi wavelength. The open circles indicate the work functions expected for one, two, three and four atomic layers of Cs on Cu(111).

We have used two different criteria to determine when full monolayer coverage is obtained. They differ by around 5% in evaporation time. The somewhat longer time is obtained from the break in the coverage dependence of $e\Phi$ when it reaches a fairly constant level after an initial steep decrease to a minimum and subsequent increase (figure 1). As an alternative we have used the evaporation time required to produce the maximum intensity for the photoemission peak due to the overlayer state characteristic of one Cs monolayer [4]. The work function values plotted in figure 1 are measured by the diode method, using the substrate work function (4.9 eV) determined by photoemission as a reference to get absolute values.

The work function increase obtained between one and three atomic layers can be understood on the basis of the theoretical work by Schulte [8] who considered a thin plane-parallel slab of jellium surrounded by vacuum. He found an oscillatory behaviour for $e\Phi$ with a thickness period of 0.5 λ_F, where λ_F is the Fermi wavelength, and with an amplitude that becomes smaller as the thickness increases (figure 2). These oscillations can be understood in simple terms. As the film is made progressively thicker, states in the potential well move to lower energies. At regular thickness intervals of 0.5 λ_F, one more state passes the Fermi energy and becomes occupied. The result is a periodic variation with thickness in the relative density of occupied states with a high energy, and thus a long tail into vacuum, and states with a low energy and a short tail. When the long tails dominate the work function is high. Due to the normalisation of the wavefunction each individual state gives a smaller contribution to the surface dipole as the thickness increases, and therefore the oscillations become attenuated as the thickness increases. To compare with Schulte's calculation we note that minimum work function values are predicted for thicknesses such that a state at $k_\parallel = 0$ coincides with the Fermi level. For Cs on Cu(111) this is very close to the situation for one atomic layer [4]. The measured value is therefore compared with the first minimum of the calculated curve showing the thickness dependence of the work function (figure 2). Experimentally the thickness can be changed only in units of one atomic layer. Since the period of oscillation, 0.5 λ_F (4.85 Å for jellium with the density of Cs), is close to the thickness, 4.4 Å, of one close-packed Cs layer, the measurement is not expected to reveal any oscillations.
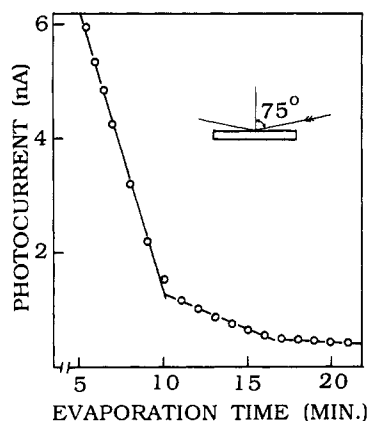
Figure 3. Photo-current from Cs-covered Cu(111) versus Cs evaporation time recorded at 2.28 eV photon energy using unpolarised light from a 0.2 mW He/Ne laser incident at an angle of around 75°.
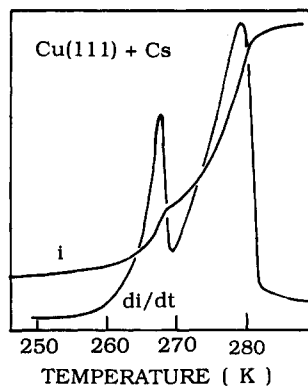

Figure 4. The photo-current and its time derivative recorded upon desorption of Cs from Cu(111) after deposition of an initial Cs coverage of three atomic layers. We associate the peaks in the derivative with the desorption of the third and the second layer. The first Cs layer remains on the surface at the temperatures used.

The Cu(111)/Cs system is not an ideal one for a comparison with Schulte's calculation. Ideally, when overlayer samples are used, the substrate should have a band gap that extends over the entire range of occupied energies and parallel wave vectors for the valence electrons in the adsorbed film. The Cu band gap at the L point of the Brillouin zone extends in energy over roughly half of the occupied Cs band and in k-space over a fifth of the area defined by the occupied parallel wave vectors. Outside the gap there are overlayer resonances rather than states with a well defined energy. The expected result of this is that the oscillations will be somewhat smoother than for a jellium slab surrounded by vacuum.

For some adsorption systems the work function varies with coverage in such a manner that the work function change, which is easily recorded, can be used as a convenient measure of the adsorbed amount [7, 8]. In the present case the work function change obtained with the diode method is nearly constant for a relatively large evaporation time interval during the formation of the second atomic layer. It would therefore appear that methods for coverage determinations based on work function changes are not of much interest. We find, however, that a quantity closely related to the work function, namely the photo-yield obtained for a photon energy slightly above the threshold for photo-emission, seems to provide a good measure of the adsorbed amount. If the photocurrent from the sample recorded for a photon energy (2.28 eV) slightly above the threshold for photoemission is plotted against evaporation time, this shows a piecewise-linear behaviour with one break after adsorption of two atomic layers and another when the third layer becomes complete (figure 3). The light is obtained from a green 0.2 mW He/Ne laser. We associate the piecewise-linear dependence found for the photocurrent with the layer-by-atomic-layer growth found for this adsorption system [4]. Also the desorption process is layer-by-layer. This is clear from the photo-current recorded when the sample is heated such that the sample temperature is increased from around 200 K to RT at an approximately constant rate. The photo-current increases in two relatively

well defined steps, the first corresponding to the current change during deposition of the third layer and the second to the change during deposition of the second layer. We therefore associate the steps in the photo-current with the desorption of the third and second Cs layers. To allow more direct comparison with the results of conventional thermal desorption spectroscopy, the derivative di/dt of the photo-current is also shown. Compared with previously reported thermal desorption spectra, the peaks in the di/dt curve are quite narrow. A narrow peak indicates that the desorption energy is well defined, and depends little on how full the layer is. The well resolved peak separation of around 12 K in figure 4 corresponds to a desorption energy difference $\Delta E_D = E_D \Delta T / T$ of around 35 meV between atoms in the second layer and atoms in the third layer. This is with $E_D = 0.80$ eV, which is the cohesive energy of Cs. Previously, multilayer desorption has been resolved and discussed extensively for adsorbed noble gases [9, 10]. We note, however, that there is also an early observation for an alkali adsorbate. When alkalis were adsorbed on different Ni crystal faces it was observed in one case, Na on Ni(100), that the desorption spectra show a doublet assigned by the authors to second- and third-layer desorption [7]. In the present case the two peaks are better resolved.

In conclusion we find that the work function of Cs adsorbed on Cu(111) varies with coverage beyond the monolayer regime. As predicted from self-consistent calculations for thin jellium films there is a modest increase of the work function as the thickness is increased from one to three atomic layers. The piecewise-linear variation of the photo-yield with coverage for photon energies just above threshold for photoemission indicates a layer-by-atomic-layer growth mode. The photo-yield can be used to measure the adsorbed amount and to follow the desorption of the alkali. The resulting desorption spectra for Cs on Cu(111) show narrow peaks corresponding to well defined desorption energies differing by around 35 meV between the second and the third atomic layer.

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