Quantum size effect in the work function of jellium slabs confined by a finite well of thickness-dependent depth

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The work function (WF) of free-standing thin jellium slabs, confined by a finite potential square well is calculated for $r_s=2.07$ (Al) and $r_s=3.25$ (Li). For given electron density the WF is a decreasing-oscillating function of slab thickness. Calculated are also WF's for one-, two-, and three-atomic-layer slabs of Al(111), Al(110), and Li(100), where values agree well with the recent *ab initio* results obtained by other authors. [S0163-1829(99)01738-5]

Quantization of the electron states normal to the thin-film surface, known as the quantum size effect (QSE), was a subject of many studies.[1,2] From the practical point of view, especially interesting are work function (WF) varations with the sample thickness L originally predicted for jellium films by Schulte.[3] This prediction has stimulated a number of theoretical studies on determination of the film size and the extent of the QSE on the WF Φ of real systems.[4] In the present paper we consider the QSE on the WF by employing a simple jelliumlike model that represents the metallic film as a finite square well, the thickness L, with the effective potential of the height $V=E_F+\Phi$, E_F being the Fermi energy (FE). For simple metals, using for WF the formula[5]

$$\Phi(k_F)=4.45\alpha\sqrt{k_F}\ \text{eV}, \tag{1}$$

one can express the barrier height as follows:

$$V(k_F)=\frac{k_F^2}{2}+0.16\alpha\sqrt{k_F}\ \text{a.u.}, \tag{2}$$

where k_F is the Fermi momentum (FM) and α is a constant equal to unity or 0.86 in dependence on the considered metal.[5] The thickness dependent FM, $k_F(L)$, determines the solution of the following equation:

$$\frac{1}{2\pi L}\int_0^{k_F} k\left[\frac{Lk}{\pi}+\frac{2}{\pi}\arcsin\frac{k}{\sqrt{2V(k_F)}}\right]dk=\frac{3}{8\pi r_s^3(L)}, \tag{3}$$

obtained, after some algebra, from the expression for the density of states, and derived in Ref. 2. In Eq. (3) the $[x]$ denotes the integer part of x, and r_s is the electron-density parameter, which for real thin metallic films depends on the film thickness L. The solution of Eq. (3), with the use of Eq. (2), gives the thickness-dependent[6] FM, $k_F(L)$, and from Eq. (1) one can calculate, for given r_s, the thickness-dependent WF, $\Phi(r_s,L)$.

Calculated in such a manner, WF varations are displayed in Fig. 1 for $r_s=3.25$ (Li) and in Fig. 2 for $r_s=2.07$ (Al). Solid curves in these figures are obtained taking in Eq. (3) the barrier height $V(k_F)$ given by Eq. (2), and the dashed one in Fig. 2 corresponds to $V=\infty$. Several notes are appropriate: First, the $\Phi(L)$ is a decreasing oscillating function of L with monotonic variation of its mean value averaged over several oscillation periods. Second, for given L, the $\Phi(r_s,L)$ is a decreasing function of r_s. Third, the changes in WF with L are greater for greater V. The present result, displayed by the dashed curve in Fig. 2, can be compared with that of Schulte obtained self-consistently for $r_s=2$ and for infinite barrier height.[3] The approximate maximum change of Schulte's (S) WF near $L/k_F=1$ (as deduced from Fig. 8 of Ref. 3) amounts to $\Phi_s(1)-\Phi_s(0.9)\simeq 0.43$ eV and the present calculations give $\Phi(1,V=\infty)-\Phi(0.8,V=\infty)=0.14$ eV, the changes are the same order in both cases. For finite barrier height $V(r_s=2.07)$, these changes reduce, however, to less than 0.1 eV.

These simple calculations cannot be, of course, compared directly with the *ab initio* computations performed for real metals. The present model can simulate however, a thin metallic slab of the thickness $L(n)$ composed of n atomic layers when it is characterized by the thickness-dependent electron density parameter $r_s[L(n)]$. The thickness $L(n)$ for $n\geqslant 2$

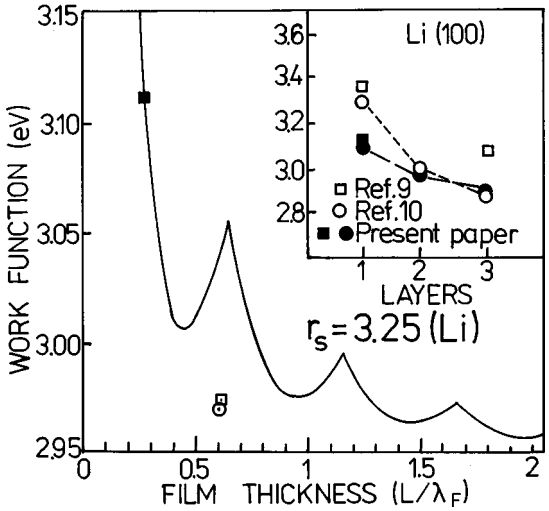

FIG. 1. Work-function variations versus L/λ_F calculated for $r_s=3.25$ (Li) (solid curve). L denotes the slab thickness and λ_F the Fermi wavelength. Full squares and full dots are the values calculated for $L_1=a_1/2$, where $a_1=6.599$ a.u. and $a_1=6.44$ a.u., respectively. Dotted square and circle represent the WF calculated for $L_1=2R_M$. Full square and dots in the inset display the WF variations with the number of atomic layers in the Li(100) slab.

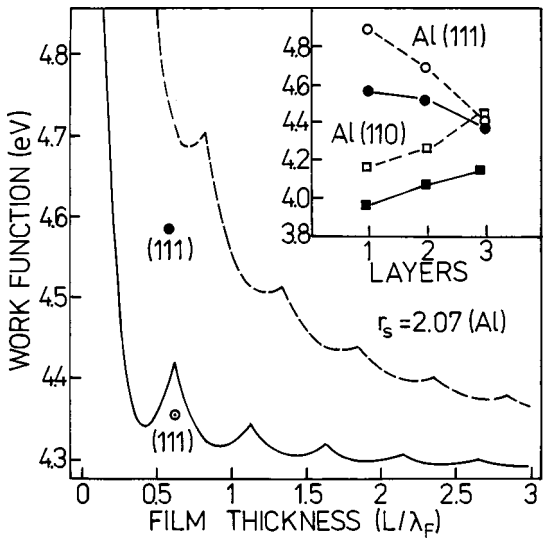

FIG. 2. The same as in Fig. 1, but for $r_s=2.07$(Al). The dashed curve represents $\Phi(V=\infty,r_s=2.07)$. Full dots and squares represent the WF calculated in the present paper for the (111)-plane oriented one-layer slab with thickness $L_1=a/2$ and with $L_1=2R_M$, respectively. In the inset, the WF variations of the $1L$, $2L$, and $3L$ of the (111) and (110) slabs marked by full circles and full squares, respectively, are compared with the WF values calculated in Ref. 4 (open circles) and Ref. 11 (open squares).

can be specified uniquely only by minimizing the total energy, however, one may try to estimate the thickness of the one-layer slab L_1 and perform calculations taking the thickness of the free-standing n-layer slab formed of n atomic (hkl) layers in the form

$$L(n)=L_1(hkl)+(n-1)d_{hkl}, \quad n=1,2,..., \tag{4}$$

where $L_1(hkl)=\lambda a_1(hkl)$ and $d_{hkl}=\delta_{hkl}a_1(hkl)$ being the distance between (hkl) planes with the lattice constant $a_1(hkl)=\beta a$. Using Eq. (4) the thickness-dependent electron-density parameter $r_s(n)$ can be expressed by the bulk one, r_s as follows:

$$r_s(n)=\beta\left[1+\frac{1}{n}\left(\frac{\lambda(hkl)}{\delta(hkl)}-1\right)\right]^{1/3} r_s, \tag{5}$$

where β is the ratio of the one-layer lattice constant a_1 to the bulk lattice constant a. For the estimation of L_1, we assume that it must be less than the nearest-neighbor distance L_{NN} in the (hkl) plane and greater than twice the radius R_M of the maximum density of the outermost electrons computed from the free-atom calculation of Herman and Skilman.[8] Therefore,

$$2R_M<L_1(hkl)<L_{\mathrm{NN}}(hkl). \tag{6}$$

The results of such model calculations are displayed in the insets in Figs. 1 and 2 for slabs with the thickness L_1, L_2, and L_3 of lithium and aluminum, respectively. Full squares [$a_1=6.44$ a.u. (Ref. 9)] and full circles [$a_1=a_{\mathrm{bulk}}=6.597$ a.u. (Ref. 10)] in the insets of Fig. 1 show the calculations performed for $L_1=a_1/2$. The *ab initio* calculated WF's are presented by empty squares (Ref. 10) and by empty circles (Ref. 9) for comparison. To compare with the WF variations computed for continuously changing slab thickness L, the full and dotted square and circle in Fig. 1 show the WF's calculated for $L_1=a_1/2$ and for $L_1=2R_M$, respectively.

Similar calculations, performed for Al(111) and Al(110) slabs, are presented in the inset in Fig. 2 by full dots ($L_1=a_1/2$) and by full squares ($L_1=\frac{3}{4}L_{\mathrm{NN}}$), respectively. Open circles and open squares represent the *ab initio* calculations by Boettger[4] and performed in Ref. 11, respectively. In the present calculations we use $a_1(111)=7.6085$ as accepted by Boettger[4] and $a_1(110)=0.983a_{\mathrm{bulk}}$ and $d_{12}(110)=0.517d_{110}^{\mathrm{bulk}}$ as was computed in Ref. 11. From the insets in Figs. 1 and 2, it is seen that the present calculations give good trends of $\Phi[L(n)]$, $n=1,2,3$, and even relatively good results, in comparison with the *ab initio* calculations.

Concluding, one can say that the variations of the work function of the ultrathin metallic slabs, found by the *ab initio* computations, can be understood on the basis of a simple model calculation of the QSE when it takes into account the variations of the Fermi wavelength with the thickness of a crystalline slab.

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