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Theory of the quantum size effect in simple metals

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Using the self-consistent pseudopotential technique and planarly averaged one-dimensional potential (quantum well), we provide a rigorous basis for understanding the quantum size effect and dimensionality of thin metal films. The density of states, work function, surface energy and vertical surface relaxations, subband energies, and surface charge density are found to vary as a function of film thickness. The density of states has a ladder-type structure (characteristic of a two-dimensional electron system); its value at the Fermi level changes in quantized steps with film thickness, L. The relative position of the Fermi level between subbands, which changes with L, provides an interesting explanation for the variation in physical properties.

Electrons confined in thin films have a quantization of states which is quite different from the bulk. The electronic wave functions normal to the plane (z direction) of the film become exponentially damped, and the energy-level spectrum splits into subbands. These and other physical phenomena arising from the lowering of the dimensionality are called the quantum size effects (QSE). They have been observed in heterostructure superlattice semiconductors[1] and have important implications, such as the Hall quantization and solid-state electronic devices with very short response time. In metals, electrons near the Fermi energy have short de Broglie wavelength (~ 5 Å), so the QSE are limited to thin films. Electron standing-wave states in thin Pb film have been observed by electron tunneling.[2] The oscillations of the chemical potential are found to influence the width of the superconducting gap.[3] Other effects, e.g., localization, can be significantly enhanced[4] in the presence of QSE.

The deposition of thin metal layers on various types of substrates leads to exotic structures and electronic properties.[5] Therefore, an understanding of the electronic properties of thin metal layers is becoming increasingly important both from fundamental and technological viewpoints. On the fundamental side one needs to be able to delineate a transition from two- to three-dimensional behavior. Also, it is important to know how the metal changes when cut to a few layers. Early studies[6] used the Sommerfeld model and treated the electron in a square cut potential to explore the QSE. Apart from these oversimplified models, Schulte[7] investigated the metal in the jellium approximation using the density-functional formalism.[8] Recently, the discrete lattice was introduced by Feibleman in a detailed linear combination of atomic orbital (LCAO) calculation.[9] Other slab calculations[10–12] have dealt with surface states and chemisorption aspects.

In this paper we present results for QSE calculated by combining the self-consistent-field (SCF) pseudopotential method and realistic model calculations. Our results are based on thin Al(111) films consisting of one, three, five, and seven layers treated by a repeating slab geometry. We performed self-consistent pseudopotential calculations[13] within the framework of a local density functional theory,[8] applied in the momentum space formalism. We used a nonlocal norm-conserving ionic pseudopotential given by Bachelet, Hamann, and Schlüter,[14] and Ceperley-Alder[15] exchange and correlation potential. Plane waves with kinetic energy less than 7 Ry are treated exactly, and those having kinetic energy between 7 and 9 Ry are included via Löwdin's perturbation scheme. During the self-consistency iterations, the electronic valence charge was sampled at 49 **k** points placed uniformly in the surface Brillouin zone. A modest amount of thermal smearing of the Fermi-Dirac distribution function was permitted to reduce the grid dependency. In addition, we generated an (x,y) averaged one-dimensional (1D) (quantum well) potential, $V(z)$, from the local part of the SCF slab potential, which is simple enough to reveal fundamental aspects of systems of lower dimensionality. We then assumed a free-electron behavior in (x,y) directions and solved the 1D Schrödinger equation numerically[16] to obtain the electronic structure of a quasi-2D system. By comparing results obtained from quantum well and SCF slab calculations we were able to draw important conclusions regarding the quasi-2D character, the dimensionality of the metal films, and provide a rigorous understanding of the QSE.

Figure 1 shows the band structure for three metal films of

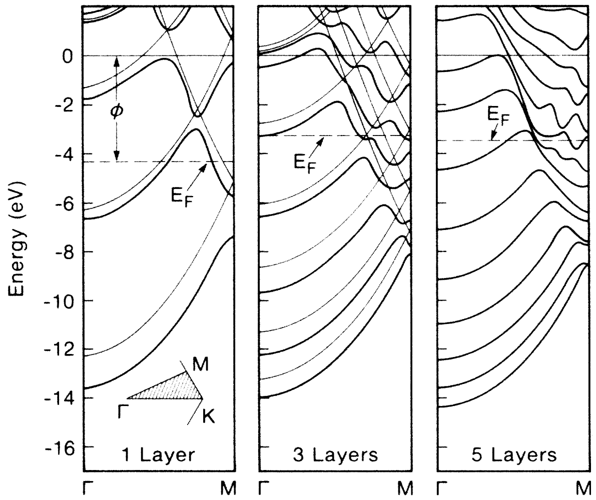

FIG. 1. Energy band structures of one, three, and five layers of aluminum, calculated by the self-consistent pseudopotential method, are shown by heavy lines. Lighter lines correspond to energy bands obtained from the quasi-2D system quantum-well structure. The energy is measured with respect to the vacuum level.

different thicknesses calculated self-consistently. Also shown is the Fermi level E_F in each case and the corresponding work function Φ which is oscillating with the film thickness.[7,9] For one and three layers, lighter lines give the subbands of the quasi-2D system described more fully below. As seen, the slab subbands and the subbands of the quasi-2D system, $E_n+\hbar^2(k_x^2+k_y^2)/2m$ follow each other closely. Some minor differences are due to the fact that the former split according to the symmetry of the slab potential. This clearly demonstrates the quasi-2D free-electron character in the thin Al film with the effective mass m^* being close to the free-electron mass m. Due to the neglect of (x,y) corrugation and the nonlocal part in the planarly averaged potential, the subbands and the Fermi level of the quasi-2D system are shifted upwards relative to that of the 3D slab. However, this 1D potential obtained by a planar avarage of the self-consistent pseudopotential is able to yield the Fermi level crossing by the subbands correctly. Hence, it is capable of providing a more realistic description of the s-p bonded metal films than a simple square well potential, as well as the jellium model. Simple models give the subband spacings $(E_{n+1}-E_n)$ to be proportional to $(2n+1)/L^2$, where the electrons are confined in a length L along z direction. A planarly averaged potential, as well as the completely self-consistent potential which we have considered here, gives a quantization quite different from $(2n+1)/L^2$, as can be seen from the irregular spacing of energy levels at Γ in Fig. 1.

It is well known that the density of states of a 2D free-electron gas, $D_2(E)$, is energy independent. Consequently, the density of states of a quasi-2D system,

$$D_{2q}(E)=\sum_n H(E-E_n)m/\pi\hbar^2$$

(where H is the Heaviside function) yields a ladder-type density of states. Thus, whenever a new subband dips

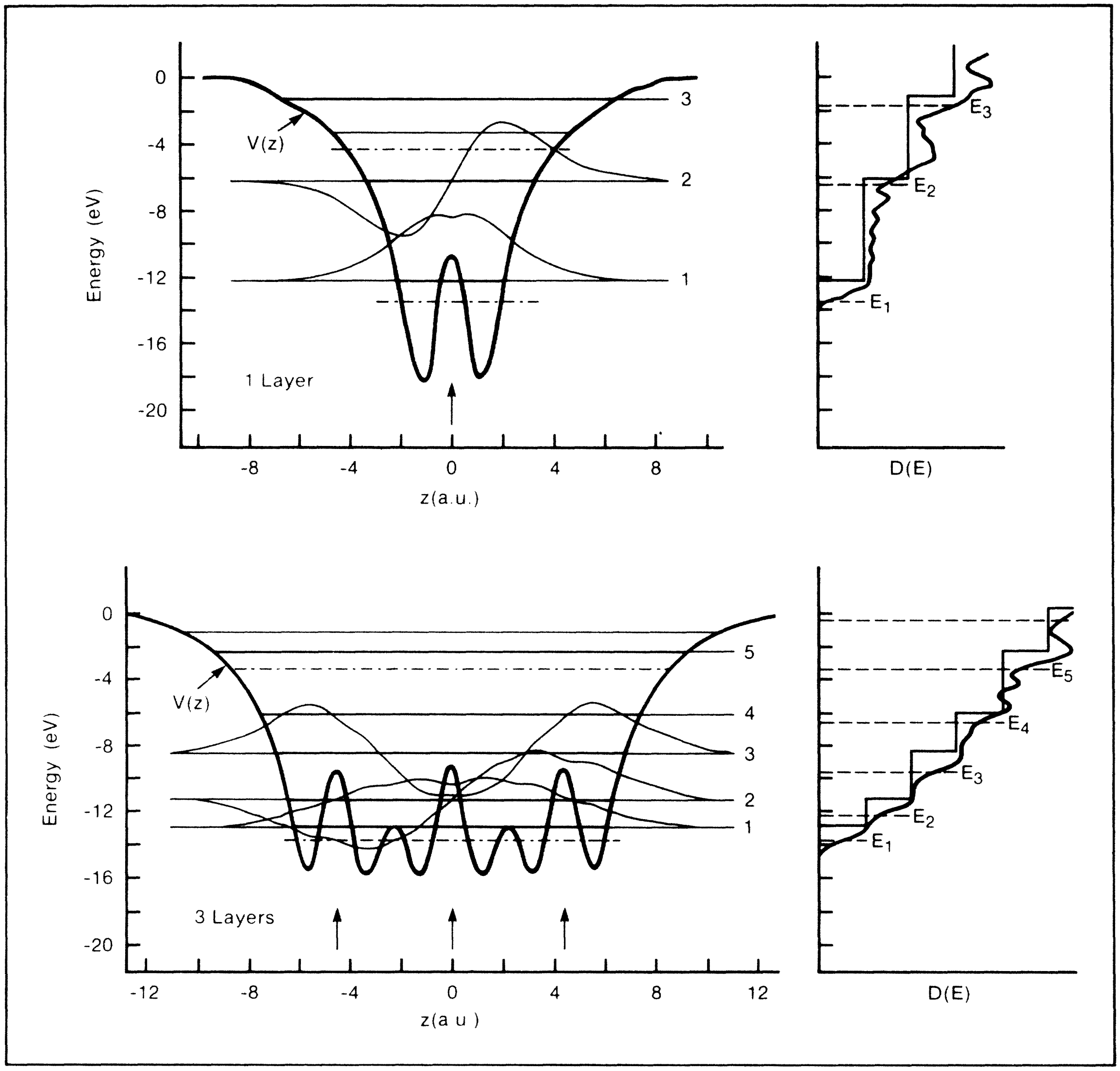

FIG. 2. 1D potentials (quantum wells) generated by the planar average of the self-consistent pseudopotentials calculated for one- and three-layer Al films. The bound subbands and the wave functions are shown. The conduction bandwidth and the energies at $\mathbf{k}=\mathbf{0}$ of the slabs are, respectively, indicated by dash-dotted and dashed lines. The ladder-type state densities of the quasi-2D system and the density of states of slabs calculated at 144 **k** points are shown in the right panels.

below the Fermi level, $D_{2q}(E)$ increases by a step $m/\pi\hbar^2$. In the limit of large L,

$$D_3(E)=\int_0^E D_2(E')D_1(E')dE'$$

becomes the density of states of a free-electron gas $\simeq\sqrt{E}$. In a real metal film, the relative positions of subbands, E_n, are closely related to the form and the symmetry of the potential, and hence $D_3(E)$ deviates from the $\sqrt{E}$ form characteristic of the density of states of the 3D free-electron gas. Since the confinement length of the electrons is finite in a thin metal film, the crossing of the Fermi level by an another subband due to an increase of L gives rise to a jump in $D_{2q}(E_F)$ causing significant changes in electronic properties. Certainly these changes are negligible for a thick film, but become important with a decreasing number of metal layers. In the jellium model, an additional subband dips below the Fermi level whenever L increases by $\lambda_F/2=(\pi/3\bar{\rho})^{1/3}$ ($\bar{\rho}$ is average charge density), and the electronic properties oscillate accordingly.[7] In the square well model potential $(E_{n+1}-E_n)$ is inversely proportional to the square of the number of layers. As stated above, in a real system the subbands are irregularly spaced, and hence, simple model potential calculations are not adequate for obtaining the Fermi-level crossing correctly.

One may also understand the properties of metal overlayers deposited on semiconductors in terms of the dependence of the subband structure on the form of the potential. When the form of this potential is changed by the substrate weakly interacting with the metal overlayer, then $D(E_F)$ may undergo a sudden change with significantly altered electronic properties. Evidently, such an effect cannot be deduced from simple quantization models. Here it may well be speculated that the superconductive state of Ag monolayer[5] on Ge bears a close relationship to the shift of the subband with respect to E_F. The density ρ_s, which is simply the number of electrons per unit area in the (x,y) plane, determines the Fermi level through the relation

$$\sum_n (E_F-E_n)=\hbar^2\pi\rho_s/m \ .$$

It is connected to the planarly averaged slab charge density by $\rho_s=\int\bar{\rho}(z)dz$. Consequently, variations in ρ_s also induce changes in the properties of the thin metal film. The electron density of the metal overlayer may vary with the geometrical structure and also the substrate temperature leading to phase transitions. It is interesting to note that the Al monolayer in Fig. 1 has an equilibrium lattice constant ($a=3.76$ Å) 7% smaller than the ideal bulk value.[17] This lattice contraction imposes an 18% change in ρ_s and a 4% increase in the work function, Φ. The bandwidth (measured from the first subband up to E_F) increases by 17%. The change of the bandwidth as a function of the lattice parameter follows the d^{-2} rule.[18] Incidentally, the calculated equilibrium total energy of Al monolayer is 0.8 eV/atom (which is twice the surface energy) higher than the bulk value. It implies that Al atoms on a substrate may prefer to form cluster rather than an epitaxial layer. However, even a weak bonding to a substrate with a binding energy $\simeq 0.8$ eV may lead to formation of epitaxial overlayer.

In Fig. 2, the calculated density of states for the quasi 2D system is shown, and it has the ladder-type structure. Also shown are the density of states of one- and three-layer films calculated at 144 **k** points in the SCF slab model. Except for some structure due to coarse **k** sampling and the lattice potential, these density of states also have a ladder shape indicating the dimensionality of the metal. We propose that the shape of the state density can be taken as a fingerprint of the dimensionality, much like the plasmon dispersion.[19] As the number of layers increases, the step density also increases, and eventually the system becomes three dimensional. This trend is already apparent in the five-layer Al slab density of states.

In Fig. 3 the surface energy, bandwidth, work function, and subband energies at $\mathbf{k}=0$ are shown for one-, three-, five-, and seven-layer slabs calculated self-consistently. Our work function and surface energy values exhibit an oscillatory behavior due to the QSE. The work function of the monolayer is large and close to the semi-infinite slab value (4.3 eV), but by going to a three-layer slab it decreases to 3.2 eV. It is interesting to note that in agreement with previous arguments, another subband drops below the Fermi level of the three-layer Al slab. In the five-layer slab, Φ increases again to 3.4 eV and reaches 3.7 eV in a seven-layer slab. As for the surface energies, they are oscillatory, but show a reverse trend as compared to Φ. Calculated forces exerted on the atoms in the ideal positions indicate small, oscillatory vertical multilayer relaxation. Small and inward direct forces on the surface layer diminish with a seven-layer film implying the size dependence of the surface vertical relaxations. Ho and Bohnen[20] found a small change in the work function ~0.2 eV between the relaxed and ideal Al(110) slab. The surface relaxation effects on the work function of the Al(111) slab are even smaller and do not effect our conclusions in any essential manner.

The oscillatory behavior of the electronic properties, especially that of the work function, is related to the surface

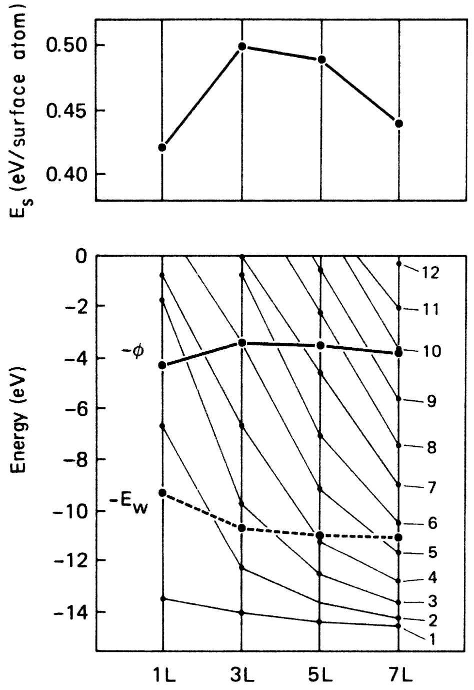

FIG. 3. Surface energies (upper panel), work function, conduction bandwidth, and subband energies at Γ (lower panel) of one-, three-, five-, and seven-layer slabs calculated by the SCF pseudopotential method.

electronic charge density varying as a function of film thickness.[7] The surface charge density is low when the Fermi level lies close to an empty subband. It passes through a local maximum when the Fermi level is near the middle of an occupied and the next empty subband. As a result, the work function is near a local minimum whenever the Fermi level is closer to a subband and increases when E_F is in between two subbands. Since the Fermi-level position with respect to subbands varies with the film thickness, the work function shows an oscillatory behavior thus described. In Fig. 3, the position of the Fermi level with respect to the subbands and oscillations in the work function confirm this argument. For example, in a monolayer the Fermi level occurs in the middle, and for three layers it is near the edge of a subband with a severe reduction in the work function. Interestingly, the Fermi level of the seven-layer thick film lies close to a subband and suggests that a six-layer film (for which E_F will be located closer to the middle) will have a higher value of the work function.

The planar average of the pseudocharge density $\bar{\rho}(z)$ has small Friedel oscillations appropriate for Al. From the outermost plane going towards vacuum, monolayer has the highest and the three-layer film has the lowest charge density among all the slabs considered here. In the multilayer slabs the highest charge density occurs in the outermost atomic plane. An analysis of the total charge density contours in the layer planes shows that the monolayer has the highest charge density at the center of the line connecting any two nearest neighbors. For multilayers, there are two maxima on the line connecting two nearest neighbors and a shallow minimum at the center of the equilateral triangles connecting the three nearest-neighbor atoms. This is a consequence of the fcc close-packed structure.

In conclusion, the self-consistent pseudopotential calculations, as well as the results from the quasi-2D system show that charge density, surface energy and surface relaxation, work function, and the conduction bandwidth, depend on the size of the metal film thickness. The relative position of the Fermi level with respect to the highest occupied and the next empty subband undergoes a change depending on the size of the film. This in turn influences the surface charge distribution and the resultant electronic properties. The relative position of the Fermi level between two subbands is an important parameter in assessing properties of metal overlayers on semiconducting substrates.[21] The calculated ladder-type density of states is characteristic of the dimensionality of very thin film and gradually goes over to the 3D system starting at around five to seven layers.

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