

“Electronic Growth” of Metallic Overlayers on Semiconductor Substrates

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We present a novel “electronic growth” model for metallic thin films on semiconductor substrates. Depending on the competition between the effects of quantum confinement, charge spilling, and interface-induced Friedel oscillations, different types of film stability are defined, as characterized by the existence of critical/magic thicknesses for smooth growth. In particular, smooth growth can be achieved only above a few monolayers for noble metals, and only for the first layer for alkali metals. [S0031-9007(98)06444-8]

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For important scientific and technological reasons, it is often desirable to prepare thin films with atomically flat interface and growth front [1]. Nevertheless, atomically flat overlayers do not grow in many heteroepitaxial systems. Recent research in thin-film growth has been focused primarily on gaining atomic-scale understanding of various kinetic processes [2,3] and stress effects [4,5]. In this Letter, we present a novel “electronic growth” model, showing that itinerant electrons can play a decisive role in defining the stability of ultrathin metal overlayers on semiconductor substrates.

In a metal film on a semiconductor substrate, the conduction electrons are confined by the vacuum on one side and the metal-semiconductor interface on the other. This produces quantum levels (or subbands) known as quantum well states. Theoretical consideration of such quantum-size effects (QSE) on the properties of thin metal films dates back to 1976, when Schulte reported that self-consistent calculations of the electronic structure of thin jellium slabs show thickness dependent oscillations in the work function [6]. Such oscillations were confirmed beyond the jellium model by Feibelman [7], who also found oscillations in the surface energy and expected the result to affect the growth of metal films. Both Schulte’s and Feibelman’s studies were for idealized freestanding metal films, neglecting possible effects of a supporting substrate. In a subsequent study of several metal-on-metal systems, Feibelman and Hamann [8] concluded that “it is unlikely that work-function QSE will be observable in a laboratory,” because the inclusion of a substrate simply washes out the quantum-size effects. Nevertheless, QSE have clearly been observed in recent studies of ultrathin metal overlayers on metal substrates [9]. In particular, Hinch *et al.* have observed unusual epitaxial growth behavior of Pb on Cu(111), and interpreted their data in terms of QSE [10].

In this Letter, we present a simple model to show how QSE can influence the stability of metal thin films on a supporting substrate, and use it to identify novel types

of film stability that are simply missing in earlier free-standing film models. Although we limit our discussion to semiconductor substrates, our approach can also be used for metallic substrates with a symmetry gap in the normal direction. This work was motivated by a recent discovery of a critical thickness beyond which atomically flat Ag films can be grown on GaAs(110) [11]. This system has long been considered to be prototypically nonwetting [12,13], and the “critical thickness” discussed here has precisely the opposite meaning used in the Stranski-Krastanov growth mode, ruling out mechanisms solely based on the stress effect.

Our model contains three central ingredients: (a) Quantum confinement, (b) charge spilling, and (c) interface-induced Friedel oscillations. Electronic confinement within the metal overlayer can mediate an effective repulsive force between the interface and the metal surface, acting to stabilize the overlayer. Electron transfer from the overlayer to the substrate, as explained below, leads to an attractive force between the two interfaces, acting to destabilize the flat overlayer. Interface-induced Friedel oscillations in electron density can further impose an oscillatory modulation onto the two previous interactions. These three competing factors, all of electronic nature, can make a flat metal overlayer critically, magically, or marginally stable, or totally unstable against roughening. Our estimates not only confirm the existence of the critical thickness for Ag growth on GaAs [11,14], but also explains the well-known fact that only the first layer of alkali metals can be smooth on semiconductors [15].

We present our theory within the framework of a general thermodynamic stability analysis, which in spirit is similar to the shell model for the existence of magic atomic numbers in metallic clusters [16]. Let $E_t(L)$ be the total energy of the system with a flat film of thickness L . $E_t(L)$ also plays the role of the Helmholtz free energy at low temperatures. The film is stable if the “compressibility” is positive, i.e., $\partial^2 E_t(L)/\partial L^2 \geq 0$. Under this condition, any small roughness in the film

tends to be suppressed when sufficient atomic mobility is provided. The film is unstable if $\partial^2 E_t(L)/\partial L^2 < 0$. In this case, the system can achieve a lower total-energy state by developing a mixed phase of different film thicknesses. A critical thickness, L_c , can be defined if the film is stable for $L \geq L_c$ but unstable for $L < L_c$ (or the other way around). Furthermore, a magic thickness, L_m , can be defined if $E_t(L)$ has a downward cusp at L_m , namely, the film is unstable on both sides of L_m . Our main task is to show when and why there can exist critical and magic thicknesses in the formation of metallic overlayers.

Here we use the simplest possible model to illustrate the central ideas, with Ag growth on GaAs(110) as the first specific example. The energy of the system is evaluated by referring to the ideal situation where the film is isolated from the semiconductor substrate by a delta function potential of infinite strength, with charge neutrality maintained on both sides of the interface, and with the interface atoms neither reconstructed nor relaxed. The vacuum levels of the film and the substrate should be equal before contact. The Fermi energy and the energy of the film $E_0(L)$ in this ideal situation are estimated by a model of a free electron gas confined by a barrier step ($W_m + E_F$) on the outer surface and by an infinite hard wall at the interface, where W_m (4.3 eV for Ag) and E_F (5.5 eV for Ag) [17] are the work function and Fermi energy (relative to the bottom of the conduction band) of the metal in bulk form, respectively. After subtracting a term linear in the film thickness, which does not change the conclusion about film stability, the function $E_0(L)$ is plotted in Fig. 1. It is seen that the energy E_0 curves up as the film thickness becomes small, showing the quantum confinement effect.

When the delta potential barrier is removed, electrons spill across the metal-semiconductor interface to lower the system energy. In equilibrium, the Fermi energy of the metal lines up with the charge neutrality level in the gap of the semiconductor [18]. For GaAs, the charge neutrality level is 0.9 eV below the conduction band edge and about 4.97 eV below the vacuum level [19]. The electron spilling leaves a layer of positive charge on the metal side with a thickness equal to the screening length l_m (0.59 Å for Ag [17]), and builds a layer of negative charge on the semiconductor side with a thickness l_s (2.8 Å for GaAs [19]) given by that of the metal-induced gap states at the neutrality level in the gap [18]. We model the interface as a capacitor, with its "plates" located at the centroids of the positive and negative charge distributions. The energy lowering due to charge spilling is then estimated as $E_c = 0.5CV^2$, where V is the initial difference between the metal Fermi energy and the charge neutrality level divided by the electron charge, and $C = \epsilon_0/(l_m + l_s/\kappa)$ is the capacitance, with ϵ_0 being the vacuum dielectric constant and $\kappa \approx 2$ [20] being the effective dielectric constant of the semiconductor near the interface. The resulting energy lowering E_c is plotted in

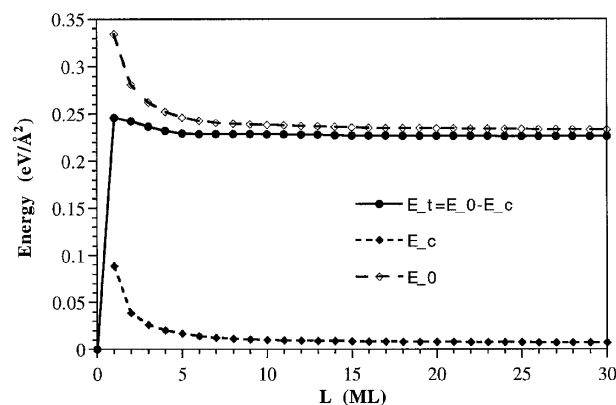


FIG. 1. Film thickness dependence of the film energies for Ag on GaAs(110). The dip at $L = 5$ ML defines the critical thickness for flat film growth.

Fig. 1, which also curves up as the thickness becomes small, because the Fermi energy of the film is squeezed higher by the quantum confinement.

The total energy $E_t = E_0 - E_c$, shown in Fig. 1, has a shape predicting the existence of a critical thickness. The energy lowering due to charge spilling has a steeper thickness dependence at smaller L , pulling the total-energy curve down. This makes the curvature of $E_t(L)$ negative in that region, rendering flat films unstable. The curvature changes sign at $L = 3$ monolayers (ML), and has a dip at $L = 5$ ML, indicating that a flat film at this thickness is particularly stable. This dip is mainly caused by the sharp energy features of the quantum well states and the Fermi surface. The curve is practically flat beyond $L = 5$ ML, showing that thicker flat films are all marginally stable. We therefore identify $L_c = 5$ ML as the critical thickness, which is of the same magnitude as the experimental finding of $L_{c,\text{expt}} \sim 7$ ML [11,14]. The agreement is satisfactory, given that the simple model does not contain any adjustable parameters, and that the absolute coverage of the film is somewhat uncertain [11,14]. Finally, notice that if we use the empirical formula $\kappa = (1 + \kappa_s)/2 = 7$ of Ref. [21], where $\kappa_s = 13$ is the dielectric constant in bulk GaAs, then the enhanced energy lowering due to charge transfer causes the change of curvature right at $L_c = 5$ ML.

The above calculations can easily be repeated for other metal-substrate systems. In these calculations, we assume that the metallic overlayer grows in close-packed form in the film thickness direction, as is the case for Ag [11,14]. Here we limit our discussions to different metals on the same GaAs(110) substrate, with comparisons of the effects of different substrates presented elsewhere [22]. The stability of Cu and Au films resembles very closely that of Ag, each with the same critical thickness of ~ 5 ML. This type of stability of an ultrathin metallic film is reproduced and designated as type A in Fig. 2 (the energies at $L = 0$ are off scale). In contrast, a qualitatively different type (type B) is obtained for the

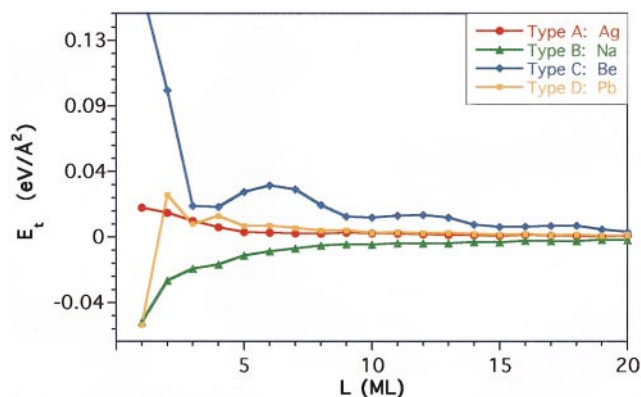


FIG. 2(color). Comparison of four representative types of film stability for different metals on GaAs, as defined in the text. Notice that an element-specific constant term has been substrated from each curve to make the total energy equal to zero at large film thickness.

alkali metals (Li, Na, K, Rb, and Cs), as represented by the case of Na in Fig. 2. Here, because of its small work function, the energy gain due to charge spilling dominates, leading to downward curving in E_t , with $\partial^2 E_t(L)/\partial L^2 < 0$. Therefore, a flat film thicker than 1 ML is unstable, because it is always possible to reduce its energy by phase separating into a rough film with smaller and larger thicknesses. This explains the well-known experimental fact that one cannot grow a smooth film of alkali metals of more than one ML on GaAs(110) [15].

We have also investigated the quantum-size effects for overlayer growth of alkaline earth metals (Be, Mg, Ca, Sr, and Ba). Unlike the alkali metals which qualitatively all follow the same curve (type B in Fig. 2), the alkaline earth metals have very different behaviors among themselves. Ca, Sr, and Ba are similar to the alkali metals (type A), but Be and Mg belong to a new type (type C), as represented by the case of Be in Fig. 2. Here, the film is magically stable around $L_m = 3$ ML; furthermore, there still exists a critical thickness at $L_c = 9$ ML above which the film is marginally stable. Calculations show that Zn and Cd also belong to type C.

A fourth type of behavior is shown as type D in Fig. 2, followed by both Al and Pb on GaAs. Here, the energy dependence is a damped oscillation with a period of 2 ML. Such oscillatory behavior has been the focus in earlier studies of quantum-size effects in either freestanding films models [6,7] or metal/metal systems [8,23].

The oscillatory thickness dependence of $E_t(L)$ for types C and D is caused by interface-induced Friedel oscillations. To illustrate this, we plot in Fig. 3 the density of a semi-infinite electron gas confined by a hard wall (the interface): $n(u)/n_0 = 1 + 3[\cos(u) - \sin(u)/u]/u^2$ [17], where $u = 2k_F z$, z is the distance from the interface, and k_F is the Fermi wave vector. For a given metal (characterized by its own k_F and interlayer spacing, d), the electron density at different layer thicknesses ($z = Ld$, with

$L = 1, 2, 3, \dots$) sample different sets of points on the same curve. If a given film thickness coincides with a minimum of the Friedel oscillations, then there is an additional energy gain, because fewer electrons need to be pushed up in energy by the confinement of the outer surface. For Na and Ag, the first (and also the deepest) minimum in the density oscillations located between 3 and 4 ML is too shallow to induce an additional magic thickness. In contrast, the first minimum for Be is large, which results in the existence of a magic thickness. For Pb, the position of the first minimum located at 1 ML coincides with the first minimum of the universal Friedel oscillation curve; this perfect phase matching in the Friedel oscillations and that due to lattice periodicity explains why, as seen in Fig. 2, the total energy at $L = 1$ ML is so low for Pb.

In the above analysis, we have neglected the energy cost associated with the creation of steps (or vertical surfaces) when we compare the energetics of a flat film and a rough film phase separated into areas of different heights. This approximation is reasonable if the length scale of the areas is much larger than the heights of the areas, because the energy gain scales with the square of the length scale of the areas, while the energy loss scales only linearly with that length scale. Moreover, we have neglected the possible growth of pyramidal and other three-dimensional structures. This temporary neglect is justified by the experimental observation that in the regime where the “electronic growth model” is operative the commonly observed pyramidal growth is replaced by the formation of islands of a magic height, with flat plateaus on top of the islands [24].

Total-energy calculations within the density-functional theory of a few selected systems, Ag/GaAs(110) and Sb/GaAs(110), allowing interlayer lattice relaxation, indeed confirm many of the salient qualitative aspects of the present theory [25]. Earlier treatments of the problem using freestanding films missed the key effects of charge transfer [6,7], without which it

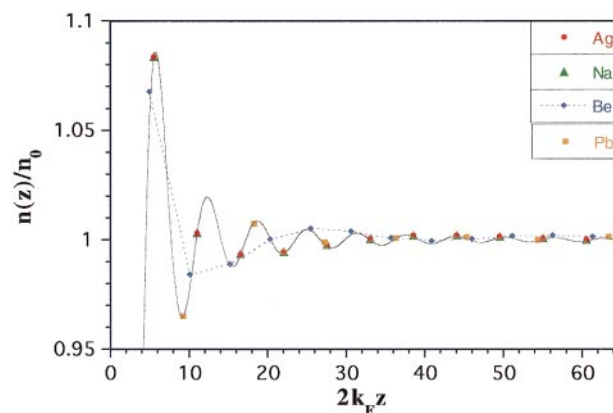


FIG. 3(color). Friedel oscillations in electron density within a semi-infinite metal caused by a hard wall located at the metal-semiconductor interface. The different metal elements sample different sets of points on the same curve.

would be impossible to define the critical thickness for Ag/GaAs.

On the experimental side, our results should provide new understanding on many existing observations in previous studies of ultrathin metallic overlayer growth on semiconductor substrates [11,14,15,22,26]. For example, the observation of critical thicknesses for smooth growth of Ag on GaAs, GaP, and GaSb [11,14,22] and the fact that only the first layer of alkali metals can grow smoothly on GaAs [15] provide strong evidences for the validity of the theory.

More importantly, one can devise new experiments to test systematically the unique predictions made here. In doing so, one should choose systems in which there is no or minimal intermixing at the interface, so as to maximize the effect of a sharp interface. For many systems, this requirement demands sufficiently low growth temperatures. Lower-temperature deposition is especially required to test the existence of the magic and critical thicknesses shown in types *C* and *D* of Fig. 2, because one typically needs to have an initial film close to the stable flat film configuration [11,14,22,26]. For systems in which such critical/magic thicknesses do exist, the morphology of the metallic overlayers can be controlled down to the atomic scale. It should also be possible to tune the values of the critical/magic thicknesses by tuning the band alignment. Therefore, the electronic growth mechanism in principle provides an important tool for quantum engineering of metallic thin films on semiconductor substrates.

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