



Surface Science Perspectives

# Quantum stability of ultrathin metal overlayers on semiconductor substrates

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Growth of metals on semiconductor substrates continues to be a major research area of the surface science and thin film growth community, for obvious reasons: metal/semiconductor interfaces are indispensable components for many device applications, ranging from metal-based transistors to interconnects. Despite many years of intensive studies, fundamental research in this area still constantly offers new excitement, with the elegant study of aluminum growth on Si(1 1 1) reported in this issue by Liu et al. [1] as a particularly poignant example.

When one element is grown on a different substrate (loosely called heteroepitaxy), the likely growth mode is typically classified into one of the three basic types: two-dimensional (2D) or layer-by-layer growth; layer-by-layer growth followed by 3D islanding; and 3D islanding. In the second mode, the 2D-to-3D transition occurs at a critical film thickness,  $t_c$ . Historically, these three fundamental growth modes have been known by the names of their respective discoverers, namely, Frank–Van der Merwe growth (FV), Stranski–Krastanov growth (SK), and Volmer–Weber growth (VW), respectively, and can be differentiated using Bauer's thermodynamic accounts based on surface and interface energy considerations [2]. Metal growth on semiconductors is heteroepitaxial in nature. Indeed, for a long while the growth modes observed in most experimental studies of metal/semiconductor heteroepitaxy had been the three modes introduced above, with no known exceptions, until the 1996 report of a new type of critical thickness,  $t'_c$ , observed for silver growth on a GaAs(1 1 0) substrate [3], below which the films are rough, and above which the films spread to

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make a very smooth, uniform layer. Now, Liu et al. [1] have found a similar growth habit for Al on Si(1 1 1). Importantly, the kinetic pathway exploited to give rise to this critical thickness in this new case is significantly different from that in the earlier example.

Already before its interesting critical thickness behavior was discovered, the growth of Ag on GaAs(1 1 0) had been widely studied. Its preferred growth mode had been well established to be the VW mode at a given temperature [4]. But a few years ago, when Smith et al. [3] applied a two-step approach suggested earlier [5] to grow silver on GaAs(1 1 0) at a low temperature ( $\sim 135$  K) followed by annealing to room temperature (RT), a new type of growth mode was discovered, qualitatively different from any of the three classical growth modes. It was found that, as the system was warmed up towards RT, the initially rough Ag film consisting of nanometer-scale 3D clusters would self-organize into an atomically smooth film. Furthermore, such a rough-to-smooth transition occurs only when the total silver coverage is equal to or exceeds six monolayers (ML) [3]. Qualitatively, the phenomenon that occurs at this newly defined critical thickness ( $t'_c$ ) is just the inverse of the transition at the critical thickness ( $t_c$ ) defined in SK growth.

Efforts to identify the physical origin of this new type of critical thickness led to the proposal of the “electronic growth” model [6]. Briefly, this model emphasizes the importance of electronic degrees of freedom in dictating the atomic arrangement and the resulting growth modes. First, the motion of the conduction electrons in the metal overlayers is confined in the direction perpendicular to the surface, and such quantum mechanically confined electron motion results in an energy contribution that helps stabilize the film against roughening. Secondly, some degree of charge spilling from the metal into the semiconductor is unavoidable, resulting in another energy contribution that destabilizes the metal film. The balance between these two defines the new critical thickness,  $t'_c$ , above which smooth growth is possible [6]. Though formulated using a very crude model (nearly free electrons in a box), the study provided a semi-quantitative interpretation of the experimental observations reported in [3]. Furthermore, the model also predicts that, for certain systems, such as Be and Pb, smooth films with singularly preferred (or “magic”) heights can be grown as a result of the interface-induced Friedel oscillations in the electron density within the metal overlayers [6]. Later it was shown that, in the ultrathin regime, the quantum size effects (QSE) can easily overwhelm the strain effects associated with the lattice mismatch between the metal film and the substrate [7]. Furthermore, a detailed study of Sb growth on GaAs(100) within density functional theory has shown that the preferred mode of growth should be bi-layers after the first/wetting layer, and the strong bi-layer preference is tied to the oscillatory variation of the density of states at the Fermi level as the film thickness increases [8].

In retrospect, different manifestations of QSE in ultrathin metal films had been suggested or observed long ago, particularly in work function, resistivity, and photoemission measurements [9]. Nevertheless, in studying Pb growth on Cu(1 1 1), Hinch et al. [10] presented perhaps the first evidence showing that the confined motion of the conduction electrons can influence the preferred mode of growth. Their helium scattering studies of Pb growth suggested the occurrence of bi-layer growth and were interpreted at that time in terms of QSE in the films, though an alternative interpretation was later proposed by some investigators from the same group [11].

Since 1999, there has been a surge in the number of experimental groups working on QSE in the growth of different types of ultrathin metal overlayers on semiconductor [12,13] and metal substrates [14], with Pb as a particularly favorable growing element [13]. Explaining precisely why Pb exhibits unusually strong QSE [15] remains a challenging issue, but a consensus has been reached from many independent studies: when grown on semiconductor (Si or Ge) or metal (Cu) substrates, Pb highly prefers bi-layer growth [13,14].

Whereas observation of bi-layer growth is being accepted as a signature of QSE in the growth of different ultrathin metal films, existence of the new critical thickness ( $t'_c$ ) that was observed in Ag/GaAs(1 1 0) [3] remains to be directly confirmed in other related systems. The absence of stable films at thicknesses less than 5 MLs in Pb growth on Si(1 1 1) has been attributed [13] to the effect of charge transfer as within the “electronic growth” model, but the thickness 5 ML is strictly speaking *not* critical, because above this, films would stabilize only for a specific set of bi-layer thicknesses.

In this issue [1], Liu et al. present convincing evidence that when Al is grown on Si(111) a critical thickness of 4 ML is observed, at or above which stable Al films can be obtained. In fact, the authors have shown that above this critical thickness layer-by-layer growth is preferred for the entire range of Al coverages studied. Also remarkably, the atomically smooth Al films at or above 4 ML were obtained by depositing the Al atoms at a low temperature (145 K) without thermal annealing, indicating that the Al adatoms have unusually high mobility at the growth front as the atoms search through the configuration space to reach a stable morphology.

In fact, maintaining a low temperature during deposition turns out to be essential for the occurrence of the newly observed transition to smooth growth, as direct deposition at room temperature results in 3D growth, characterized by the formation of large faceted islands [1,3,4]. The reason is: too much mobility at the growth front would result in an initial configuration that is too far away in configuration space from the atomically smooth configuration defined by the QSE.

In analogy to the observations reported in Ref. [3], Liu et al. attribute the physical origin of the existence of the new type of critical thickness for smooth growth to the confined motion of the conduction electrons with the Al films. This interpretation is certainly very plausible, given the formation of quantum well states in Al films grown this way (clearly observed by angle-resolved photoemission spectroscopy [16]), and the huge influence these quantum well states can have on the film stability (as emphasized in the “electronic growth” model [6,7]).

Collectively, the work by Liu et al. and previous studies by others in this expanding area lead one to consider the appealing notion of “quantum engineering” to produce exciting new forms of matter: It is indeed becoming possible to devise kinetic pathways along which quantum mechanics is playing an essential role as one engineers atomically smooth metal overlayers, metal/semiconductor junctions, and other low-dimensional structures (such as quantum wires and metal nanoclusters) for microelectronics applications.

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