Quantum Electronic Stability of Atomically Uniform Films

D.-A. Luh,1,2 T. Miller,1,2 J. J. Paggel,3 M. Y. Chou,4 T.-C. Chiang1,2*

We have studied the structural stability of thin silver films with thicknesses of N = 1 to 15 monolayers, deposited on an Fe(100) substrate. Photoemission spectroscopy results show that films of N = 1, 2, and 5 monolayer thicknesses are structurally stable for temperatures above 800 kelvin, whereas films of other thicknesses are unstable and bifurcate into a film with N = 1 monolayer thicknesses at temperatures around 400 kelvin. The results are in agreement with theoretical predictions that consider the electronic energy of the quantum well associated with a particular film thickness as a significant contribution to the film stability.

Structures and devices of nano-dimensions have useful and possibly unique properties (I), and an important issue for practical applications is structural stability. As the physical size of a system approaches atomic dimensions, quantum effects are likely to play a significant role. Here we demonstrate that quantum electronic effects are likely to play a significant role. Here we demonstrate that quantum electronic effects are likely to play a significant role.

1Department of Physics, University of Illinois at Urbana–Champaign, 1110 West Green Street, Urbana, IL 61801–3080, USA. 2Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana–Champaign, 104 South Goodwin Avenue, Urbana, IL 61801–2902, USA. 3Freie Universität Berlin, Institut für Experimentalphysik, 14195 Berlin, Germany. 4School of Physics, Georgia Institute of Technology, Atlanta, GA 30332–0430, USA.

To whom correspondence should be addressed. E-mail: chiang@mr.lulu.edu
sharp quantum-well peaks, whose positions are indicative of the film thicknesses (8, 9). Emission spectra for the 6-ML film show that, as the sample temperature \( T \) increases, the 6-ML peak begins to broaden thermally (Fig. 1, left). As \( T \) rises above \( \sim 320 \) K, the peak intensity rapidly decreases, and two new peaks emerge simultaneously. These new quantum-well peaks derive from film thicknesses of 5 and 7 ML. Thus, the original 6-ML film bifurcates into two adjacent-integer-monolayer thicknesses. After the film temperature is increased to more than 500 K, the film is allowed to cool to 115 K (bottom spectrum), and the resulting sample is predominantly a mixture of \( 6 \pm 1 = 5 \) and 7-ML thicknesses.

The data for an initial film thickness of 3 ML (Fig. 1, right) show a similar behavior. At the end of the heating cycle, the film has mostly bifurcated into a mixture of \( 3 \pm 1 = 2 \) and 4-ML thicknesses. The relative intensities of the peaks are not necessarily a good indication of the surface area covered by each thickness, because the photoemission cross sections of quantum-well peaks are strongly dependent on the photon energy and film thickness (10). The 4-ML peak sits almost exactly on the Fermi level, and its intensity is significantly cut off by the Fermi-Dirac distribution function. All films studied for \( N \) up to 15, except for \( N = 1, 2, \) and 5, bifurcate in a similar manner at temperatures around 400 K. The exceptional cases are \( N = 1, 2, \) and 5—are much more stable. Films with \( N = 5 \) are stable up to the highest temperature, 900 K, used in our experiment. The \( N = 1 \) and 2 films are stable to over 800 K.

The threshold temperature for film instability can be determined by monitoring the photoemission intensity of the quantum-well peak while ramping the sample temperature upward. Examples of such temperature scans (Fig. 2) demonstrate a sharp drop in intensity as the film geometry begins to change. Results from such measurements for \( N \) up to 15 are shown in Fig. 3A. The result for the stable film thickness at \( N = 5 \) represents a lower bound, and the data point is simply the highest temperature that the film has been subjected to. Multiple data points are shown for several thicknesses as an indication of the degree of reproducibility.

Because the electronic states in such films are quantized, there can be considerable monolayer-by-monolayer variation in total electronic energy, depending on where the Fermi level cuts off the occupancy of these states. The quantum-well levels near the Fermi level are exclusively of the free-electron–like \( sp \) character for the Ag films. Their energies \( E \) are determined by the bulk band structure and the boundary conditions that are tied to the phase shift function \( \Phi(E) \). The relevant equation is the Bohr-Sommerfeld quantization rule (8–10)

\[
2k_x(Nt + \Phi(E)) = 2n\pi
\]

where \( k_x \) is the component of the momentum perpendicular to the film surface, \( k_x(E) \) is determined by the band structure, \( t \) is the monolayer thickness, and \( n \) is a quantum number. To model the present system, we used a realistic band structure based on the combined interpolation scheme (11). For simplicity, the \( 4d \) bands of Ag are removed from the calculation. These bands are located \( 4 \) eV below the Fermi level and are fully occupied. An experimentally determined phase-shift function \( \Phi(E) \) (8) is used, which yields quantum-well state energies at the surface Brillouin zone center in excellent agreement with the experiment.

Equation 1 is easily generalized to quantum-well states with finite \( k_x \) and \( k_z \). Each quantum number \( n \) is thus associated with a subband (10). Such subbands are nearly parabolic near the surface zone center, but the exact dispersions are determined by the band structure and can deviate substantially from nearly-free-electron behavior near the (111) neck of the Ag Fermi surface. Our calculation incorporates the full \( sp \) band structure, and it would be interesting to explore whether or not the (111) neck, or departure from a spherical Fermi surface, has an important effect on the film stability. The total electronic energy \( A(N) \) of the system is computed from a sum of all of the occupied states below the Fermi level within the first surface Brillouin zone. The quantity relevant to stability against \( N \rightarrow N \pm 1 \) bifurcation is the energy difference defined as

\[
\Delta(N) = \frac{1}{2}(A(N + 1) + A(N - 1)) - A(N)
\]

which is just one-half of the discrete second derivative of \( A(N) \). A large positive \( \Delta(N) \) corresponds to a stable film. The results of our calculation (Fig. 3B) show that \( N = 2 \) and 5 are particularly stable, in agreement with the experiment.

The above calculation does not extend to \( N = 1 \), because \( A(0) \) is ill-defined. Changes in geometry for a monolayer film must be accompanied by exposure of the substrate Fe surface, which has a much higher surface energy than Ag (12). Ag nominally wets an Fe surface based on this surface-tension consideration, and this probably accounts for the stability of the monolayer film.

The high stability for \( N = 5 \) can be understood in terms of the quantum-well state energies at the surface zone center. The energy spacings between quantum-well states are generally smooth, monotonic functions of \( N \). As mentioned above, a film thickness of \( N = 4 \) yields a quantum-
well peak very close to the Fermi level at $E = 0$. Increasing the quantum-well width to $N = 5$ causes this state to drop below the Fermi level. This becomes the topmost-occupied quantum-well state for $N = 5$, and it is unusually deep below the Fermi level relative to the other cases (see Fig. 1). The whole subband has, on average, a lower energy, leading to an overall lower energy for the system. This argument suggests that film stability is mainly determined by the quantum-well state energies at the surface relative to the Fermi level. This is similar to the issue of stability for clusters and nanowires, which prefer structures with a closed electronic shell. For Ag films considered here, adding one atomic layer generally leads to the addition of a partially occupied subband. The $N = 5$ case is an exception. Without a new subband below the Fermi level, it resembles a shell-closing point. Its topmost subband below the Fermi level is relatively deep, leading to a highly stable film. In going from clusters to wires and to films, the dimensionality of confinement is reduced from three to two and then to one. For films, the energy continuum in the other two dimensions tends to diminish this shell-closing effect. Nevertheless, quantum variations in stability remain an important effect, as shown in this study.

The dominant issue for film stability is thus the phase-shift function $\Phi$, which directly affects the quantum-well energies. In the present case, photoemission measurements provide an accurate determination of $\Phi$, which is critical to the quantitative analysis presented above. Simple models based on one-dimensional potential wells, adopted in previous studies of metal films on semiconductors (5), generally do not lead to accurate quantum-well levels and are thus unable to explain our results quantitatively. Other effects that are important for metal-semiconductor interfaces, including an interface capacitor term (5), are found to be unimportant in the present case of a metal-metal interface. Using atomically uniform films in our experiment, questions regarding multiple steps do not arise, and the issue of stability reduces to a simple $N \rightarrow N \pm 1$ bifurcation as the first step toward roughening. For rough or nonuniform films, the situation can be far more complex, as there can be a multitude of paths for film-morphology evolution, including, for example, step bunching and pyramid formation.

A general strategy for stability engineering in nanostructures is thus to tailor the geometry to minimize the energies of the occupied states relative to the Fermi level. This is similar to the issue of stability for clusters and nanowires, which prefer structures with a closed electronic shell. For Ag films considered here, adding one atomic layer generally leads to the addition of a partially occupied subband. The $N = 5$ case is an exception. Without a new subband below the Fermi level, it resembles a shell-closing point. Its topmost subband below the Fermi level is relatively deep, leading to a highly stable film. In going from clusters to wires and to films, the dimensionality of confinement is reduced from three to two and then to one. For films, the energy continuum in the other two dimensions tends to diminish this shell-closing effect. Nevertheless, quantum variations in stability remain an important effect, as shown in this study.

**Proposed Square Spiral Microfabrication Architecture for Large Three-Dimensional Photonic Band Gap Crystals**

Ovidiu Toader and Sajeev John

We present a blueprint for a three-dimensional photonic band gap (PBG) material that is amenable to large-scale microfabrication on the optical scale using glancing angle deposition methods. The proposed chiral crystal consists of square spiral posts on a tetragonal lattice. In the case of silicon posts in air (direct structure), the full PBG can be as large as 15% of the gap center frequency, whereas for air posts in a silicon background (inverted structure) the maximum PBG is 24% of the center frequency. This PBG occurs between the fourth and fifth bands of the photon dispersion relation and is very robust to variations (disorder) in the geometrical parameters of the crystal.