Quantum Electronic Effects on the Properties and Growth of Thin Films and Nanostructures

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The electronic structure of a thin film is modified relative to the bulk by the presence of the film's boundaries. In systems with well-ordered interfaces, the component of the electronic wave vector perpendicular to the film becomes quantized due to confinement, and the continuum of states characteristic of the bulk is replaced by a discrete set of quantum well states or subbands. This quantization leads to changes in electronic structure, and the physical properties can be very sensitive to the system dimensions and boundary conditions. This article reviews recent investigations of such quantum size effects in atomically uniform metallic films of Ag on Fe(100) and Pb on Si(111). Atomic-layer-by-atomic-layer variations in properties, including thermal stability, work function, electron phonon coupling, surface energy, and internal structural distortion are measured by photoemission and x-ray diffraction. The results are correlated with the measured changes in electronic structure, and are compared with simple model predictions and first-principles calculations. Issues related to morphological evolution during growth and annealing are also examined and explained in terms of a surface energy function which can be determined directly from an analysis of the film thickness distribution of a thermally roughened film.

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I. INTRODUCTION

Thin films with thicknesses in the nanometer range can exhibit interesting and useful structures and properties markedly different from the bulk counterparts due to geometric confinement of electrons. The underlying quantum physics is a cornerstone for nanoscale science which is a broadly based interdisciplinary enterprise highly relevant to the advancement of materials, devices, and technologies. Quantum electronic effects are particularly important for metallic films in which cutoff of the electronic occupation at the Fermi level leads to substantial variations in electronic structure. For semiconductor films, by contrast, the effects of lattice strain are often more important. This paper reviews some recent results in two model systems, Ag on Fe(100) and Pb on Si(111), that demonstrate quantum electronic effects in metallic films. In both cases, atomically uniform films can be prepared. These highly ideal films provide an excellent platform for precision measurements. Com-
parison with predications and calculations based on either simple models or first-principles methods leads to a detailed understanding of the underlying scientific principles.

Angle-resolved photoemission is employed to probe the electronic structure in these systems. Geometric confinement of electrons leads to the formation of discrete states. In a sense, thin films are just like atoms or molecules, but with adjustable dimensions. These discrete states, commonly referred to as quantum well states, shift in energy as a function of film thickness and can cross the Fermi level. Such crossings lead to sharp changes in the electronic density function. Per density functional theory, the ground state of the system is a unique functional of the electron density function. The physical properties, depending on the ground state wave function, are thus expected to change sharply at such crossings. This paper reviews recent measurements of work function, electron-phonon coupling, thermal stability, and surface energy, which show quantum-size variations generally in agreement with this picture.

Confinement of electrons and boundary effects can also lead to Friedel charge oscillations in real space. Such oscillations are damped and have a dominant spatial Fourier component at $2k_F$ (twice the Fermi wave vector). The atomic lattice of the film responds to the charge oscillations and can become distorted. This lattice distortion is expected to be proportional to the derivative of the charge distortion, and should exhibit damped oscillations as well. An x-ray reflectivity measurement of Pb films on Si(111) illustrates this effect.

Thermal stability of a system is related to its total energy. The atomically uniform films mentioned above are mostly metastable. Depending on the growth condition and annealing history, films can develop preferred or magic heights, roughness, and self-assembled nanostructures. The morphological evolution generally depends on both energetics and kinetics, and the results can be very rich. In one experiment, the roughening effect of high temperature annealing of initially smooth Pb films deposited on a Pb-terminated Si(111) surface is examined. The resulting film morphology is expected to mostly reflect the energetics. An absolute determination of the surface energy as a function of the film thickness (or island height) can be made this way, as illustrated by an in situ x-ray diffraction study of the evolution of film morphology. In another experiment, x-ray diffraction studies of the growth of Pb on Si(111)-(7×7) reveal a novel growth behavior that can be attributed to surface phase separation as a result of global system energy minimization.

II. EXPERIMENTAL METHODS

The main techniques employed in this research include angle-resolved photoemission and x-ray diffraction. The photoemission work was performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison in Stoughton, Wisconsin. Several beamlines and two endstations were employed for the work described herein. The x-ray diffraction work was carried out at the UNICAT beamlines, Advanced Photon Source, Argonne National Laboratory. A surface diffraction chamber attached to beam line 33-ID was used for all of the measurements to be discussed below. Detailed information about each experiment
and the procedures for sample preparation can be found in the cited publications. For Pb films on Si(111), two types of Si substrates were used. In some measurements, the Si(111)-(7×7) surface was employed. For the rest, the Si(111)-(7×7) surface was first terminated by Pb to form a \((\sqrt{3} \times \sqrt{3})R30^\circ\) reconstruction before film deposition. In all cases, film deposition was performed at low temperatures.

III. RESULTS AND DISCUSSION

III-1. Quantum Well States in Atomically Uniform Films

Significant work on quantum well states in thin films appeared in the literature already in the 70’s [1–3]. Our group reported in 1986 direct observation by angle-resolved photoemission of quantum well states in films with the film thickness as a controlling parameter [4, 5]. A detailed discussion of the basic physics of quantum wells from the perspectives of angle-resolved photoemission can be found in several recent review articles [6-8].

Quantum well states in films arise as a result of confinement of valence electrons, and appear as discrete peaks in angle-resolved photoemission spectra. The thickness of a film is quantized. As it increases from \(N\) to \(N+1\) monolayers (ML), the observed quantum well peaks should jump discontinuously. However, most results reported in the literature do not show such discrete layer behavior, and the measured peak widths are rather large. These problems are caused by film roughness. Our group discovered in 1998 that Ag films could be prepared with atomic layer perfection on Fe (100) [9, 10]. This finding, unexpected and surprising at that time, has enabled highly accurate measurements of the electronic structure of films. Through a systematic study of the thickness dependence, electronic effects associated with the surface, the interface, and the bulk can be separately extracted. The results have significant implications regarding the kinetics and energetics of film growth. Ag/Fe(100) is an excellent atomic-scale laboratory, and this system has been a major platform for our research in the past several years.

Fig. 1 shows normal emission spectra for Ag coverages of 38, 38.5, and 39 ML. The 38-ML spectrum shows a set of quantum well peaks. So does the 39-ML spectrum, but the peak positions are different. The 38.5-ML spectrum shows two sets of peaks, which are well represented by a linear combination of the two sets for 38 and 39 ML. This discrete atomic layer resolution, observed for thicknesses over 100 ML, establishes that the films are uniform on an atomic scale. A tight control and accurate knowledge of the film thickness are important for precision measurements. Roughness can lead to peak broadening and analysis error. In our study, the absolute film thickness is deduced by atomic layer counting.

III-2. Interferometric (Phase) Analysis

An analysis based on the time-reversed LEED formalism shows that quantum well states can be treated as stationary states or cavity modes in an electron interferometer [10]. The photoemission line shape for an \(N\)-ML film is given by the Fabry-Perot formula (Airy
FIG. 1: Normal emission spectra taken from 38, 38.5, and 39 ML of Ag on Fe(100).

function)

\[ I \sim \frac{1}{1 + \frac{4f^2}{\pi^2} \sin^2(kNt + \frac{\Phi}{2})}, \]  

(1)

where \( k \) is the wave vector related to the energy \( E \) through the dispersion relation, \( \Phi \) is the combined surface and interface phase shift, and \( t \) is the monolayer thickness. The quantity \( f \) is the finesse (ratio of peak separation to peak width) given by

\[ f = \frac{\pi \sqrt{Re^{-Nt/\lambda}}}{1 - Re^{-Nt/\lambda}}, \]  

(2)

where \( R \) is the combined surface and interface reflectivity, and \( \lambda \) is the mean free path (related to lifetime). Eq. (1) yields a set of quantum well peaks at

\[ 2kNt + \Phi = 2n\pi, \]  

(3)

where \( n \) is a quantum number. This is the Bohr-Sommerfeld quantization rule (phase accumulation rule). An analysis of the spectra over a wide range of thickness yields the band structure, phase shift, reflectivity, and lifetime width, as shown in Fig. 2. The band structure obtained is the most accurate to date, with a deduced Fermi wave vector more accurate than the de Haas-van Alphen value [11, 12].

A fundamental assumption leading to Eqs. (1) and (3) is that the Bloch wave vector \( k \) is a good quantum number and is related to the energy through the bulk band dispersion relation. This is an excellent approximation for simple metals, where the electronic screening length roughly equals the atomic radius. Because of the very short screening length, the electronic structure can be well described by a local Hamiltonian. An electron propagating in a film senses the same bulk Hamiltonian except when it is very close to the boundaries. The wave vector \( k \) is thus well defined within the film except near the boundaries, and the phase shift \( \Phi \) accounts for the boundary effects.
III-3. Thermal Stability

A fundamental issue in nanoscale science and technology is thermal stability. This can be affected by quantum size effects, as demonstrated by a study of Ag/Fe. Each quantum well state as seen in Fig. 1 corresponds to a subband which disperses as a function of $k_\parallel$. From photoemission results, we can compute the total electronic energy of the system by summing over all occupied states. Cutoff at the Fermi level of subband occupancy gives rise to significant monolayer-by-monolayer variations in total electronic energy. Such variations affect the thermal stability \[13\].

Experimentally, each film is ramped up in temperature until its morphology changes. Films with thicknesses of $N = 1, 2$ and $5$ ML are stable to temperatures over 800 K, while other films for $N$ up to 15 begin to bifurcate at $T \sim 400$ K into adjacent-integer-monolayer thicknesses, as illustrated in Fig. 3 for $N = 6$ and 3. The large variations in bifurcation temperature are summarized in Fig. 4(a). The quantity relevant to stability against bifurcation is the energy difference,

$$\Delta(N) \equiv \frac{1}{2} [A(N + 1) + A(N - 1)] - A(N), \quad (4)$$

where $A(N)$ is the total electronic energy. This is proportional to the discrete second derivative of $A(N)$. A large positive $\Delta(N)$ corresponds to a stable film. Fig. 4(b) shows the results of our calculation (not applicable for $N = 1$). Indeed, $N = 2$ and 5 should be particularly stable, in agreement with the experiment. These results are related to the “magic thicknesses” in films, atomic packing effects in nanowires, and stability of nanowires reported in the literature \[14–19\]. Our results can be understood in terms of a one-dimensional analog.
FIG. 3: Spectra for Ag/Fe(100) with initial thicknesses of 6 and 3 ML. The spectra, from top to bottom, were taken at increasingly higher temperatures, with the bottom spectra taken after the sample had cooled off.

FIG. 4: (a) Temperature at which a Ag film with an initial thickness of $N$ becomes unstable and begins to bifurcate. (b) Calculated energy difference against bifurcation.

of the shell effect for elements in the period table. A recent first-principles total-energy calculation yields consistent results [20]. The same first-principles calculation for a free-standing film shows markedly different results, demonstrating the importance of boundary effects.

III-4. Quantum Oscillations of Physical Properties

Per density functional theory, the ground state of a system is a unique functional of the electron density. Each time a subband edge crosses the Fermi level as the film thickness
varies, the electron density function changes abruptly, and the physical properties should change correspondingly. Such changes generally follow a damped oscillatory behavior as a function of $N$, with a functional form resembling Friedel oscillations. The oscillation period can be found from Eq. (3). Taking the difference between two consecutive crossings ($\Delta n = 1$) at the Fermi level yields the period of oscillation as

$$\Delta N t = \frac{\pi}{k_F} = \frac{\lambda_F}{2},$$

or one half of the Fermi wavelength. This is the same oscillation period for magnetic coupling in multilayer systems exhibiting the giant magnetoresistance (GMR) effect [21]. For Ag(100), the period is 5.8 ML. This is a dominant contribution to the variations in physical properties, but there can be others.

Fig. 5 presents an illustration of the oscillatory behavior. The data represent the work function of Ag/Fe (100) for $N = 0 \sim 15$. Subband crossings of the Fermi level are marked by arrows, and these correspond approximately to the experimentally observed work function variations [22]. Also shown are results from first-principle calculations. A complication is that the Ag and Fe lattices are slightly mismatched. In one calculation (labeled “unstrained”), the Fe substrate is artificially slightly expanded to conform to the unstrained Ag film lattice. This is presumably a good approximation for thicker films. In the other calculation (labeled “strained”), the Ag film is assumed to be slightly compressed to conform to the Fe lattice; this situation would be more relevant at small film thicknesses. The calculations reproduce the main features of the data.

The electron-phonon coupling of the quantum well states also exhibits oscillatory variations, as shown in Fig. 6 [23]. As the temperature increases, the quantum well peaks
broaden due to increased phonon scattering. The rate of increase in peak width is related to the coupling strength, known as the electron-phonon mass enhancement parameter:

$$\lambda = \frac{1}{2\pi k_B} \frac{d\Delta E}{dT}.$$  \hspace{1cm} (6)

Fig. 6 shows a close correspondence between the experimental results and a model calculation. The oscillations are superimposed on a \(\sim 1/N\) decay pattern. This \(1/N\) dependence results in a very large \(\lambda\) at small thicknesses, which can be attributed to an interface effect. A large \(\lambda\) is often associated with a high superconducting transition temperature within the BCS model. Our observation suggests an interesting possibility of enhanced or novel superconducting behavior in thin films. Ag in the bulk form is not superconducting. For Ag on Fe, the chance of finding superconductivity is probably slim because Fe is ferromagnetic. Substrates made of nonmagnetic materials are better candidates for exploration of thin film superconductivity.

III-5. Film Growth, Morphology, Stability, and Energetics of Pb on Si(111)

We discovered recently that atomically uniform films of Pb can be grown on Si(111) despite a large lattice mismatch [24, 25]. Fig. 7 presents normal emission photoelectron spectra taken from Pb films grown on a Pb-terminated Si(111) surface. The discrete peak evolution indicates atomic layer uniformity at integer monolayer thicknesses. It is interesting to note that sharp quantum well peaks are seen only for odd \(N = 5, 7,\) and 9. In this
FIG. 7: Photoemission intensity as a function of film thickness and binding energy for Pb films on a Pb-terminated Si(111) surface.

system, the period of quantum oscillations is 2.2 ML, implying a nearly bilayer modulation of properties. Thus, films with even \( N \) are expected to be markedly different from films with odd \( N \). However, over a sufficiently wide range of \( N \), the phase of the even-odd oscillations can reverse because the period is not exactly 2 ML. The result is a beating pattern with a period of 9 ML superimposed on the bilayer oscillations.

A measurement of the thermal stability of the films reveals that films with \( N = 6 \) and 8 are much more stable than the neighboring odd thicknesses \( N = 5, 7, \) and 9. This observation agrees with the bilayer oscillations. The film with \( N = 4 \) is, however, not as stable. This is because the case of \( N = 4 \) is very close to a nodal point of the 9-ML beating pattern, where the phase for even-odd oscillations reverses. This beating pattern is revealed in a direct measurement of the surface energy as a function of \( N \) to be discussed below.

The internal layer structure of each film can be affected by quantum size effects [26]. Confinement of the electrons leads to Friedel oscillations in the charge density within the film. The resulting charge imbalance about each atomic plane yields a force that distorts the lattice, which can be quantified by x-ray measurements. Unlike electron diffraction and STM which are primarily surface probes, x-rays have a large penetration depth, allowing structural determination for all atomic layers in a film. Fig. 8 shows x-ray reflectivity of Pb films of various thicknesses prepared on Pb-terminated Si(111). A striking feature is the enhancement of “1/2-order” peaks (marked by triangles) in-between the Pb Bragg peaks, indicating an approximately bilayer modulation of the internal atomic layer structure, in agreement with expectation.

A direct measure of the film energetics has been made by annealing a smooth film of Pb prepared on Pb-terminated Si(111) to high temperatures [27]. The film roughens, and x-ray measurements yield the relative population \( p_N \) of thickness \( N \). Fig. 9 shows the evolution. The initial film (bottom curve) is fairly smooth. As the temperature rises, the roughness increases with preference for certain thicknesses. The final distribution is rather broad, and the even-odd oscillations in \( p_N \) and the beating pattern are apparent. The
FIG. 8: X-ray reflectivity of Pb films grown on a Pb-terminated Si(111) surface. The numbers indicate the nominal film thickness in monolayers.

FIG. 9: Percentage surface coverage of layer thickness $N$ for Pb on Si(111) as a function of $N$ and annealing temperature.
quantity \( p_N \) relative to the local average \((p_{N-1} + p_{N+1})/2\) is related to the surface energy through the Boltzmann factor. An analysis yields the absolute surface energy shown in Fig. 10, which exhibits the bilayer oscillations and the beating pattern.

All of the work described so far for Pb films was done on Pb-terminated Si substrates.
FIG. 12: (a) Calculated relative surface energy per surface atom for freestanding Pb films as a function of $N$. (b) The same for Pb films on Si. In each case, the dotted curves represent envelope functions for the quantum oscillations based on a simple analytic fit to the calculation.

The results are noticeably different for Pb growth on Si(111)-(7×7). It is difficult to prepare atomically uniform films with small $N$. The difference can be attributed to the different boundary conditions. In one experiment, we grew Pb on Si(111)-(7×7) at 180 K. The growth process was monitored in situ and in real time by x-ray measurements of the Pb (10$L$) truncation rod [28]. The results show that the initial growth is a flat wetting atomic layer, followed by the formation of islands of a fairly uniform height of 5 ± 1 ML above the wetting layer (for a total island height of 6 ML, including the wetting layer thickness). These islands then grow to fill the surface, and layer-by-layer growth takes over on further deposition. The growth sequence is shown schematically in Fig. 11. Such growth behavior is rather unusual, but is qualitatively consistent with reports of certain preferred heights based on STM and diffraction work of other groups. What is puzzling is that the magic height of 6 ML bears no obvious relations to the 2.2 ML oscillation period and the 9 ML period for the beating pattern expected for the Pb films.

Fig. 12 shows the results from first-principles model calculations of the surface energy per atom for the Pb/Si system [28, 29]. Pb and Si are not lattice matched. A full calculation with two incommensurate in-plane lattice constants is not yet feasible. The calculation is carried out instead with the Si compressed by 8.8% to conform to the Pb lattice constant, at the expense of possible errors. A similar calculation is also carried out for freestanding Pb films without the Si substrate. For both the freestanding and supported films, the results exhibit Friedel-type damped oscillations with a period of oscillation of 2.2 ML. The beating pattern is indicated by the dotted curves, obtained by a fit to the theoretical results using an analytic asymptotic form of the Friedel function. The main difference between the freestanding and supported films is the phase of the beating function, which depends...
on the boundary conditions. The close agreement between the first-principles calculations and the simple model fits is not surprising, as Pb is a nearly free electron metal.

For the supported films, the surface energy shows a deep minimum at $N = 6$, in addition to the absolute minimum at $N = 1$. The absolute minimum at $N = 1$ favors the formation of a wetting layer at this thickness. For coverages between 1 and 6 ML, the system can phase separate by spontaneous decomposition into a linear combination of $N = 1$ and 6 to lower the system energy. The dashed line in Fig. 12(b) represents the energy of the phase-separated system, which is lower than the original curve. Thus, the observed magic island formation at $N = 6$ can be attributed to this phase separation effect.

Growth kinetics could potentially hinder the phase separation and trap the system in other nearby local minima, such as the one at $N = 4$. However, the thermal energy $k_B T$ at the growth temperature, indicated in Fig. 12(b) by a vertical bar, is comparable to the other shallower minima, and trapping appears to be a relatively minor effect. This is consistent with the observation that the islands form as soon as the wetting layer is complete, which further implies rapid and facile diffusion of adatoms on the surface and over the island edges. Thus, the system is in a quasi-equilibrium condition at the growth temperature. At higher coverages beyond the phase-separation region, the quantum variations in surface energy diminish rapidly, and the system maintains a nominal layer-by-layer growth in order to minimize step and kink energies.

As discussed above for Ag/Fe in connection with Eq. (4), the most relevant quantity for thermal stability is the second derivative of the system energy. This stability criterion is a local one. Namely, one is concerned with the variation in system energy right around the initial configuration, with a focus on the tendency for the system to bifurcate ($N \rightarrow N \pm 1$), which is the first step toward film breakup. The system can evolve further after bifurcation toward configurations with even lower energies, with possible hindrance by kinetic barriers. For Pb growth on Si(111)-(7×7) as discussed above where the system morphology under a quasi-equilibrium condition is concerned, the more relevant quantity is the global energy landscape. These examples illustrate that both the local stability and the global energy landscape can play important roles in film evolution and growth. The effects of kinetics and barriers must be considered for a complete description of the system behavior.

IV. SUMMARY

This review summarizes some recent experimental and theoretical results in connection with quantum size effects in metallic films. Examples are drawn from two model systems, Ag on Fe(100) and Pb on Si(111). In each case, the films can be prepared with atomic-level uniformity under appropriate conditions, thus offering opportunities for precision measurements and detailed analyses in terms of models and first-principle calculations. Through examples, it is illustrated that the physical properties of the films, including the work function, electron-phonon coupling, thermal stability, and surface energy can exhibit atomic-layer-by-atomic-layer variations. The internal atomic layer structure of a film can also be affected by electron confinement, resulting in a distortion reflective of the Friedel
charge oscillations. Surface and interface effects can become quite important at small film thicknesses, and certain properties, such as the electron-phonon coupling, can be significantly enhanced. A change in boundary condition may lead to significant consequences, as illustrated by theoretical calculations and by experiments in which different surface terminations are used. Issues of growth and film morphology evolution caused by annealing are examined and analyzed in terms of local features and the global landscape of the surface energy function.

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