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Atomic-layer-resolved quantum oscillations in the work function: Theory and experiment for Ag/Fe(100)

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The work function of atomically uniform Ag films grown on Fe(100) is measured as a function of film thickness. It shows layer-resolved variations as a result of quantum confinement of the valence electrons. A first-principles calculation reproduces the observed variations except for very thin films (one and two monolayers), and the differences can be attributed, in part, to strain effects caused by the lattice mismatch between Ag and Fe. These results illustrate the close interaction between interface effects and surface properties.

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The properties of a solid can be substantially modified as its physical dimensions are reduced to the nanoscale. Such quantum-size effects are well known, and have been studied extensively in connection with the modification of bulk properties.[1] Much less familiar but equally important is the modification of surface properties. The present work examines a basic surface property in a simple system, the work function of a film, as a function of the film thickness. An elementary picture of the work function involves a surface dipole layer that a valence electron must overcome in order to escape. Since the screening length in a metal is rather short (~0.5 Å), one might expect a minimal influence of the film thickness on the work function. However, the quantum confinement of the valence electrons in a film can result in quantum-well states.[2–4] That is, the crystal momentum along the direction perpendicular to the film becomes discretized. This leads to changes in the electronic density, including Friedel-type oscillations. The work function, as with many other properties, is a functional of the electronic density, and should similarly exhibit quantum variations. As the thickness of a film increases, more subbands of quantum-well states become occupied. The density of states at the Fermi level undergoes an abrupt change each time a new subband crosses the Fermi level, and the work function should correspondingly exhibit a small, but noticeable, cusp. These periodic cusps as a function of film thickness were first demonstrated by Schulte in a self-consistent calculation for a jellium slab.[5] The theoretical treatment was later extended by various authors to include atomistic effects, and to incorporate more accurate methods of calculation.[6–9]

In addition to its relevance as an important element in our understanding of surface science, a modified, or tunable, work function can be useful for applications such as catalysis, because a slight change in the energy scale is exponentially amplified for chemical reactions.[10] Despite the interest, there exists yet no definitive experiment to verify and test the basic theoretical concepts. The main experimental challenge is that most films are far from being ideal. Atomic steps and associated film thickness variations are common, which would smear out the quantum variations and, worse yet, modify the work function through the roughness-induced Smoluchowski mechanism.[11] In the present work, we examine Ag(100) films grown on a Fe(100) whisker. This system, with a fcc-on-bcc epitaxial relationship, represents a nearly ideal atomic-scale laboratory as atomically uniform films can be grown over a macroscopic area and over a wide range of film thickness.[12,13] Our measured atomic-layer-resolved work function, indeed, shows clear quantum variations in the form of a series of cusps. While it is gratifying that the existing theoretical concepts prove to be qualitatively correct, it is important to push the theory further for a quantitative comparison. To this end, we have carried out a large-scale first-principles calculation incorporating the substrate, ferromagnetic Fe, in a realistic manner—the effects of the substrate prove to be important. The measured layer-by-layer variations in work function are well reproduced in this calculation except for the thinnest films (one and two monolayers). The discrepancy at these small thicknesses can be attributed, in part, to lattice strain caused by the lattice mismatch between Ag and Fe (0.8%). These results illustrate the level of accuracy and detail achievable with modern experimental and theoretical methods for fundamental surface and film studies.

In our experiment, atomically uniform Ag films with coverages of N monolayers ($N=1,2,...,23$) were prepared by a low-temperature deposition and annealing procedure.[12,13] The films were examined with angle-resolved photoemission at the Synchrotron Radiation Center in Stoughton, Wisconsin, using an undulator beamline equipped with a four-meter normal-incidence monochromator. The system resolution was set to 20 meV. Quantum-well states appeared as a series of sharp peaks in normal emission, and their energy positions were a measure of the absolute film thickness. A coverage slightly less than N monolayers would result in spectra with major peaks corresponding to N monolayers and additional minor peaks corresponding to $N-1$ monolayers. This condi-

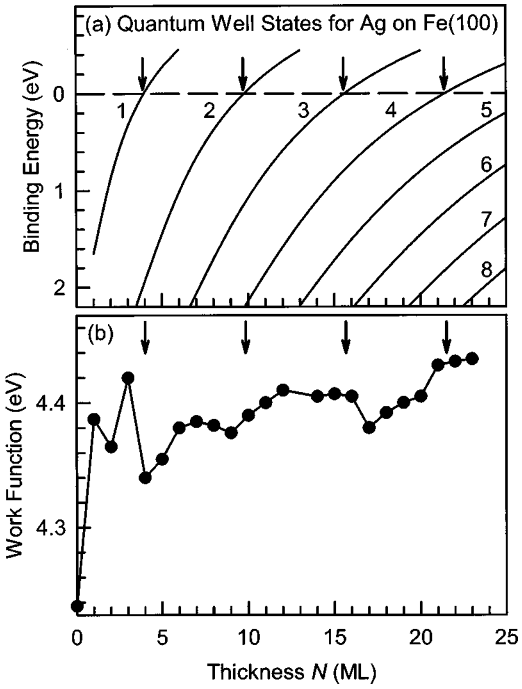

FIG. 1. (a) Binding energies of quantum-well states at $\bar{\Gamma}$ for Ag films on Fe(100) as a function of thickness N in terms of monolayers. The continuous curves are model interpolation of the experimental results obtained at discrete values of the film thickness. The quantum number is shown for each branch. The arrows indicate the points at which the various branches cross the Fermi level. (b) The measured work function (circles) connected by lines for clarity. The arrows in (a) are reproduced.

tion, when present, was corrected by additional Ag deposition to bring the total coverage to N monolayers. The work function of the sample was determined, with a precision of ±5 meV, by measuring the position of the vacuum cutoff in photoemission, with the sample biased by a battery to a small negative voltage to give an initial boost in velocity for the electrons that leave the sample surface at zero kinetic energy.

Figure 1(a) shows the evolution of the binding energies of the quantum well states at the zone center $\bar{\Gamma}$ as a function of the film thickness N, plotted as continuous curves.[14] As expected, the energy spacings between neighboring curves become smaller as N increases. Thus there are more occupied states at larger N. Associated with each of these states at the zone center is a subband with a positive effective mass for dispersions parallel to the surface plane. The numbers 1–8 in the figure are the quantum numbers or the subband indices. The four arrows indicate where the bottoms of the subbands cross the Fermi level, and the periodicity of this crossing, $\lambda = 5.8$ monolayers, is determined by[4]

$$\lambda = \frac{\pi}{k_{\Gamma X} - k_F},$$

where $k_{\Gamma X}$ is the distance between the zone center and the X point in the Brillouin zone, and $k_F = 0.828 k_{\Gamma X}$ is the Fermi wave vector for Ag(100).[14]

In accordance with the general argument presented above, a sharp change in the density of states at the Fermi level occurs at each of these crossing points, and a cusp in the work function is expected. The measured work function is shown in Fig. 1(b) as circles connected by lines for clarity. Significant layer-by-layer variations are evident. The four arrows in Fig. 1(a) are reproduced here, and there are indeed cusps in the data, but the correspondence is only approximate. In addition, there is a slow rising trend toward larger N, and a sharp cusp at $N = 2$ that cannot be explained in terms of Fermi level crossing of the quantum-well states. Even at $N = 23$, the measured work function has not yet reached a saturation value corresponding to bulk Ag(100).

To move beyond the qualitative argument presented above and to verify in detail the quantum origins of the oscillations, we have carried out first-principles calculations using the Vienna Ab-initio Simulation Package (VASP) based on density-functional theory with ultrasoft pseudopotentials and plane waves.[15] The generalized gradient approximation[16] with spin polarization is incorporated in this calculation, which is necessary to yield the correct ground-state crystal structure for Fe. To maintain the periodic boundary condition we adopt a symmetric slab geometry in which the substrate is modeled by ten layers of Fe atoms covered by Ag films of N monolayers on both sides. Therefore, only Ag films are exposed to vacuum, which is represented by a region of free space equivalent to 12 layers of Ag(100) planes. To keep the numerical problem manageable, the small interfacial lattice mismatch between Ag and Fe is neglected by using a slightly altered lattice constant in the calculation. In one calculation, the lattice constant of the substrate Fe is set to the theoretical value for bulk Fe itself (2.85 Å, based on the same method of calculation, which is 0.6% less than the experimental value), and the Ag film is thus slightly strained. In another calculation, the Fe substrate lattice constant is set to be commensurate with the theoretical Ag lattice (nearest-neighbor distance of 2.94 Å). The Ag film is thus unstrained at the expense of a slightly strained substrate. In each case, the positions of the substrate atoms are fixed in the calculation, while the Ag layers are allowed to fully relax in the vertical direction. The changes in Ag interlayer spacing are found to be quite small, of the order of 1%. Numerical convergence is carefully checked to ensure a high degree of precision. The energy cutoff of the plane waves is chosen to be 237 eV, and the k space is sampled over a $20 \times 20 \times 2$ grid. The work function is determined by the difference of the Fermi level and the local potential at the center of the vacuum region. The rather large size of the supercell presents a challenge, and the computation is limited by available memory to a maximum of 10 ML of Ag on each side of the Fe slab. Many papers on thin film physics are based on simplified models.[5–9] To show that the boundary effects are important, we have also performed, for comparison, a calculation without the Fe substrate to yield results for free-standing, unstrained Ag films.

Figure 2 shows a comparison of the experiment with the theoretical results for free-standing Ag films. The agreement is quite poor. About all one can say is that there is a minimum at $N = 4$ and a maximum at $N = 7$ that are in agreement

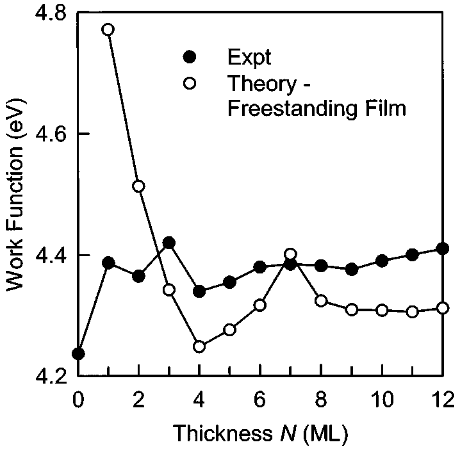

FIG. 2. The measured work function (filled circles) and the calculated work function for free-standing films (open circles).

with the experiment. Thus this calculation for free-standing films is not a good representation of the real system, and implies that the boundary condition at the interface has a large effect on the surface properties. Indeed, the agreement is vastly improved for the case of unstrained Ag films on a slightly strained Fe substrate as presented in Fig. 3(a). Ignoring the points for $N=0-2$ for now, the shape of the experimental curve is well reproduced by the calculation, including the two minima at $N=4$ and 9, marked by vertical dashed lines in the figure, and a broad hump in between. The overall offset, at less than 0.1 eV, is not a serious concern here. This type of calculation, while quite capable of predicting the size-dependent variations, is less accurate at predicting the absolute values. Part of the problem is related to the use of a finite vacuum region in the supercell. The potential in the middle of this vacuum region has not yet fully decayed to the value at infinite distance.

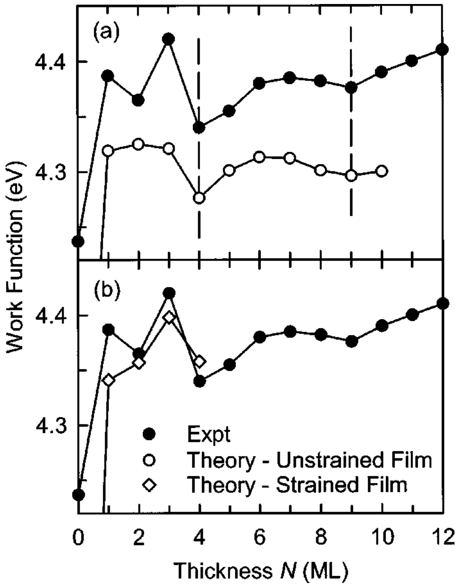

FIG. 3. (a) The measured work function (filled circles) and the calculated work function (open circles) for Ag films at the theoretical in-plane Ag lattice constant on an Fe substrate slightly strained to conform to the Ag lattice. (b) The measured work function (filled circles) and the calculated work function (open diamonds) for Ag films with an in-plane lattice constant strained to conform to an unstrained Fe substrate.

One possible source for the discrepancy at $N=2$ and below is strain effects. Films this thin are likely strained to conform to the substrate lattice, while thicker films are strain relieved. To explore this possibility, Fig. 3(b) presents a comparison of the experimental results with the calculation in which the Ag film is strained to be commensurate with the Fe substrate. Ignoring a possible overall offset as before, the point at $N=2$ becomes much lower than the point at $N=3$, with a difference very close to the experiment. The qualitative behavior of the work function for strained Ag films with more layers than those shown in Fig. 3(b) is not expected to be different from that for unstrained Ag films since the strain effect has a short range. Thus the good agreement between theory and experiment is extended down to $N=2$. The two points at $N=1$ and 0 are still off, though. In particular, the point at $N=0$, which is the work function of bare Fe(100), is very different from the experimental value. The calculated work functions are 3.7 and 3.9 eV for the strained and unstrained Fe substrates, respectively, which are much lower than the experimental value of 4.24 eV. This kind of discrepancy in the electronic structure calculation is actually not surprising. That is, even with the best methods available to date, it is difficult to make an accurate, absolute prediction of the surface properties. The overall offset mentioned above for Ag, at less than 0.1 eV, is an example. This kind of inaccuracy becomes much larger for Fe partly due to complications caused by ferromagnetism, and results in a much lower theoretical value at $N=0$. It is likely that the same effect, at a greatly reduced magnitude, also affects the point at $N=1$, where the theoretical value is also lower than the experimental value, but the magnitude of the discrepancy is substantially smaller.

To sum up, we have investigated a macroscopic surface property, the work function, for Ag films on Fe(100) as a function of film thickness. These films are prepared with atomic-layer perfection in order to achieve atomic layer resolution and to facilitate comparison with first-principles calculations. The experiment constitutes a detailed, quantitative measurement of this kind. The basic physics of the work-function variation involves quantum confinement of the valence electrons, which leads to a modification of the overall electronic structure. While certain general features can be predicted based on simple arguments, the details depend sensitively on the boundary condition at the interface. Thus calculations based on a free-standing film geometry do not agree with the experiment. The substrate must be included in the modeling for a quantitative agreement. Despite the very small lattice mismatch between Ag and Fe, evidence is presented for the influence of strain caused by the lattice mismatch. These results present a stringent test of our current experimental and theoretical capabilities in regard to thin film and quantum well studies and point to areas for future improvement.

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