## Effects of the substrate on quantum well states: A first-principles study for Ag/Fe(100)

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We have studied the properties of quantum well states in supported Ag(100) films on the Fe substrate by first-principles density-functional calculations. The energies of these quantum well states as a function of thickness N are examined in terms of the characteristic phase shift of the electronic wave function at the interface. These energy-dependent phase shifts are determined numerically for both the film-substrate and film-vacuum interfaces. It is also found that the substrate has a major effect on film stability, enhancing the stability of the N=5 film and reversing that of the N=2 film.

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Quantum confinement of electrons in a metal thin film results in the so-called quantum well (QW) states<sup>1</sup> with discrete crystal momenta in the direction perpendicular to the film. These electronic states have been the subject of numerous experimental investigations in recent years because of the critical role they play in determining many interesting properties of the film. For example, in growing metal thin films or nanostructures on a substrate, the QW states are found to be responsible for producing the unexpected flat-top islands with "magic" heights,<sup>2-4</sup> for generating an unusual growth pattern,<sup>5</sup> and for the thickness-dependent stability<sup>6</sup> observed in the experiment. The QW states also give rise to an oscillatory work function as the thickness varies,<sup>7</sup> and thus affect the details of the surface adsorption processes.<sup>8</sup> Moreover, the QW states are directly connected to the oscillation in the exchange coupling between two magnetic materials across a nonmagnetic spacer layer of various thickness,<sup>9</sup> and to giant magnetoresistance.<sup>10</sup> Therefore, the characterization and understanding of the formation of the QW states is crucial in providing a quantitative description of these intriguing phenomena. Since the confinement is provided by both the substrate and the vacuum, the specific interface invariably affects the level positions and needs to be considered explicitly.

Experimentally the energies of the QW states can be measured by photoemission,<sup>1,9</sup> inverse photoemission,<sup>11</sup> and scanning tunneling spectroscopy (STS).<sup>2,3</sup> The results are usually analyzed using a picture of standing waves within a potential well, in which an energy-dependent phase shift upon reflection at the interface is included. The quantization condition (or the phase accumulation model) yields<sup>12,13</sup>

$$2k(\varepsilon)Nd + \Phi_1(\varepsilon) + \Phi_2(\varepsilon) = n2\pi, \tag{1}$$

where k is the perpendicular wave vector for energy  $\varepsilon$  in the bulk, N the number of layers, d the interlayer spacing, and n an integer.  $\Phi_1$  and  $\Phi_2$  are energy-dependent phase shifts of the electronic wave function upon reflection at the two boundaries. They are related to the logarithmic derivatives of the wave function at the interface. In a rather concise way the phase shift represents a system-dependent confinement effect by the substrate or vacuum. For a lack of theoretical calcu-

lations for realistic systems, a simple WKB expression or a convenient ansatz is often employed for these phase shifts in the literature.<sup>1,9</sup>

The purpose of this work is to investigate these aforementioned issues through first-principles calculations for a representative system in order to shed light on the nature of the QW states, the effect of the substrate, and consequently the size-dependent properties. Ag on Fe(100) is chosen because of the existence of extensive high-quality experimental data. In addition, the small lattice mismatch (less than 1%) for fcc Ag on bcc Fe in the [100] direction justifies the use of commensurate slabs in the calculation. Previous calculations of this system employed the tight-binding model<sup>13</sup> and the layer-Korringa-Kohn-Rostoker method,14 with an emphasis on the energies of the QW states. In this paper we will focus on the influence of the substrate on the energies of these quantum well states, their interfacial phase shifts, and the stability of the films. In order to make comparisons, similar calculations are also performed for freestanding Ag(100)films.

The calculations are carried out using the Vienna ab initio simulation package (VASP)<sup>15</sup> based on density-functional theory (DFT) with ultrasoft pseudopotentials<sup>16</sup> and plane waves, with the Ag d orbitals included as valence states. The generalized gradient approximation<sup>17</sup> with spin polarization is employed in order to obtain the correct ground-state crystal structure for Fe. Our calculated lattice constant for Ag is slightly larger than the experimental value by about 1.6%. The substrate is modeled by ten layers of Fe covered by Ag films of various thicknesses in the [100] direction. To keep the calculation feasible, the small lattice mismatch is ignored by using the Ag lattice constant for the slab. For the calculation of the work function, the Fe substrate has to be covered by Ag films on both sides so that only Ag films are exposed to vacuum.<sup>7</sup> For the present study of the energy levels of QW states, the configuration with the Fe substrate covered on one side is sufficient because of the strong confinement for these QW states. Periodic slabs separated by a vacuum region equal to 12 Ag layers are used. The Brillouin zone summation is performed with a  $20 \times 20 \times 2k$ -point grid and the plane-wave energy cutoff is 237 eV. The k-point convergence of the total energy is carefully tested and the error is estimated to be of the order of a few meV per surface



FIG. 1. Calculated energies of minority-spin quantum well states at  $\overline{\Gamma}$  as a function of thickness for freestanding (open circles) and supported (filled circles) Ag(100) films at the experimental lattice constant. Also shown (stars) are the measured values from photoemission experiments (Ref. 18). The energy zero is set at the Fermi level and the solid lines through the data points are a guide to the eye. The quantum numbers *n* are also indicated for the three topmost branches.

unit cell at most. Relativistic effects are included at the scalar level and numerical convergence in the energy and force is carefully checked. Vertical layer relaxations are found to be small: the outmost interlayer separation has a small contraction of less than 2% compared with the perfect bulk value, and the second interlayer distance expands only slightly (less than 1%).

The QW states in the Ag film result from the confinement by the vacuum on one side and by the hybridization gap of the Fe substrate on the other. Because of the *s*-*d* hybridization in Fe, the two *s*-like bands of the  $\Delta_1$  symmetry in the [100] direction are separated by a finite energy. Within the energy range of this gap the *s* band in Ag, also of the  $\Delta_1$ symmetry, cannot penetrate into the Fe substrate, leading to an effective confinement. The hybridization gap in the minority-spin band structure of the Fe substrate used in the calculation is found to be in the range of -2.4 to 1.8 eV with respect to the Fermi level. Thus, the existence of the QW states near the Fermi energy and their energy variation across the Fermi level as a function of film thickness give rise to interesting size-dependent properties.

Figure 1 shows the energies of the QW states at  $\Gamma$  as a function of film thickness for both the freestanding and supported (100) films. They are calculated at the experimental lattice constant. The energy zero is set at the Fermi energy of each film. As expected, the energies of the QW states are bounded by the top of the Ag bulk band at the Brillouin zone boundary, which is located at 1.61 eV in our calculation. For the supported films, we identify the minority-spin QW states by examining the plane-averaged charge density along the film direction for every eigenstate in the slab calculation. In Fig. 1 the solid lines through the data points are intended to guide the eye, which separate the QW states into branches as labeled in the figure. The quantum number *n* in Eq. (1) is

chosen in such a way that it represents the number of nodes of the QW states inside the film. As we can see from Fig. 1, there is a noticeable difference between the energies of QW states in the freestanding and supported films. The difference is larger for thinner films and becomes smaller for thicker films. This can be understood from Eq. (1) in which the first term dominates for large N, namely, the boundary condition becomes less important. Therefore, the energy difference in Fig. 1 between the QW states of freestanding and supported films becomes smaller for thicker films. On the other hand, at a given thickness the difference is larger for larger binding energies. This feature will be explained later in the discussion.

In bulk Ag, the Fermi level cuts through the calculated  $\Delta_1$ band at a position of  $0.173\pi/d$  measured from the zone boundary, in excellent agreement with the value of  $0.172\pi/d$ measured by QW photoemission spectroscopy<sup>18</sup> and the value of  $0.181 \pi/d$  by the de Haas-van Alphen measurement.<sup>19</sup> Using Eq. (1) it can be shown that a new branch is expected to cross the Fermi level for every incremental increase in the film thickness of about 1/0.173(5.8)layers in Fig. 1. Although the energies of the QW states for freestanding and supported films are different for a given N because the phase shifts are different in Eq. (1), the periodicity in N for their QW states to drop below the Fermi level stays the same in Fig. 1. The energies of the QW states in Ag/Fe(100) as measured by most recent photoemission experiments<sup>18</sup> for atomically uniform films are also shown in Fig. 1. The agreement between theory and experiment is excellent. The calculated energies for unoccupied OW states are also in reasonable agreement with the measured values by inverse photoemission<sup>11</sup> and two-photon photoemission<sup>20</sup> (not shown). Moreover, every time a new branch crosses the Fermi level (for example, near N=4 and 10), the work function shows a local minimum (cusp) at this location.<sup>7</sup> This is due to the fact that the states near the Fermi level has a larger leak of charge out of the film, giving rise to a stronger dipole near the surface.

To examine the extent of confinement, we have plotted in Fig. 2 the plane-averaged charge densities of the four QW states shown in Fig. 1 for the N=8 freestanding and supported films, respectively. Atomic planes are indicated by dotted lines and only five out of the ten Fe layers are shown. According to Fig. 1, two of these four states are above the Fermi level and two are below. For the supported film, the charge density does decay quickly into the substrate, indicating a clear confinement. A direct correspondence is found between the QW states in the supported films and those in the freestanding films. The characteristics of these QW states can be understood in terms of a rapid oscillation described by the quantum number n and an envelope function of a longer period.<sup>1,11</sup>

Using the energy data points in Fig. 1, one can deduce the sum of the interfacial phase shifts,  $\Phi_1 + \Phi_2$ , for the QW states using Eq. (1) and the bulk band structure. For the freestanding film,  $\Phi_1 = \Phi_2$  and one can obtain the Ag-vacuum phase shifts directly. They are plotted as open circles in Fig. 3. Since the energy range of interest is quite far from the calculated vacuum level of 4.3 eV, this phase shift curve



FIG. 2. Plane-averaged charge densities of four representative minority-spin QW states in N=8 freestanding (left) and supported (right) Ag(100) films. Atomic planes are indicated by dotted lines and only five out of the ten Fe layers are shown.

is nearly featureless for most of the energy range, except for the feature near the top of the band. A simple expression obtained from the WKB approximation is often used in the literature and has the form<sup>21</sup>

$$\frac{\phi(\varepsilon)}{\pi} = \sqrt{\frac{3.4 \text{ eV}}{\varepsilon_v - \varepsilon}} - 1, \qquad (2)$$

where  $\varepsilon_v$  is the vacuum level. Equation (2) is plotted as a dashed curve in Fig. 3. Compared with the current calculated values (open circles), a shift of about  $0.2\pi$  is found below the Fermi level. For the supported films, only the sum  $\Phi_1 + \Phi_2$  in Eq. (1) can be deduced, and the data are represented by filled circles in Fig. 3. This curve is in good agreement with the result deduced from photoemission measurements,<sup>18</sup>



FIG. 3. Interfacial phase shifts of QW states for the Ag-vacuum (open circles) and Ag-Fe (crosses) interfaces. The former are deduced directly from calculations for freestanding films. The latter are obtained by subtracting the Ag-vacuum contributions from the calculated sum of the two interface phase shifts for supported films (filled circles). The WKB expression of Eq. (2) is plotted as the dashed line and the result deduced from a fit to the photoemission data (Ref. 18) is shown by the solid line.



FIG. 4. The inverse of the energy spacing of quantum well states near the Fermi level in freestanding (open circles) and supported (filled circles) Ag films as a function of thickness.

shown by a solid line. Note that the data points within a given energy range can come from films of very different thickness. Both of the datasets for freestanding (open circles) and supported (filled circles) films vary smoothly as a function of energy with little scattering, indicating that Eq. (1) does determine the energies of the QW states quantitatively, provided the interfacial phase shifts are known.

Taking the difference of the two sets of data (open and filled circles) in Fig. 3, we can obtain the phase shifts for the Ag-Fe interface, shown by crosses in the figure. It is often assumed in the literature using a simple step-potential model that the interfacial phase shift changes by  $\pi$  across a gap. In contrast, the current result yields a value that is much larger. This results from the fact that we have attributed all interface effects (including the modification of the potential at a real interface) to this single parameter, therefore the value is not necessarily constrained between 0 and  $\pi$ . Another interesting feature is that the difference between the phase shifts of the Ag-vacuum and Ag-Fe interfaces gets larger as the binding energy increases. Therefore, according to Eq. (1), for a fixed thickness the energy difference between the QW states associated with freestanding and supported films would become more noticeable for states with larger binding energies. This feature can be easily identified in Fig. 1.

The energies of QW states near the Fermi level can be measured by STS experiments. One quantity that is often presented in these measurements is the approximate level spacing  $\delta E$  near the Fermi level. Taking the derivative of Eq. (1) with respect to energy and evaluating it at the Fermi level for a given *N*, we have

$$\frac{1}{\delta E} \approx \frac{2d}{hv_F} N + \frac{1}{4\pi} \left[ \Phi_1'(\varepsilon_F) + \Phi_2'(\varepsilon_F) \right], \tag{3}$$

where  $v_F$  is the Fermi velocity obtained from the slope of the bulk band at the Fermi level and  $\Phi'(\varepsilon_F)$  the energy derivative of the interface electronic phase shift at the Fermi level. Therefore, the measured  $1/\delta E$  curve should be a linear function of *N*, with a slope connected to  $v_F$  and independent of the type of interfaces. Figure 4 shows the calculated results for the freestanding and supported Ag films using energies in Fig. 1. Indeed the two curves follow a straight line and have the same slop, with kinks located at the positions where new branches of QW states cross the Fermi level. Note that the intersection of the linear curve with the horizontal axis is not necessarily at N=0, due to the nonzero energy derivative of the interfacial phase shifts at the Fermi level.

Even though the confinement takes place only in one of the three dimensions, the stability of the film could also be affected due to the variation in the electronic energy.<sup>22</sup> For example, we can see from Fig. 1 that the N=4 supported film has a QW state right at the Fermi level, while the last occupied QW state in N=5 has a very low energy. Thus the N=5 film is expected to have an exceptionally low electronic energy, and therefore a high stability. We use the second difference of the total energy as a measure of the relative stability of an N-layer film with respect to the films of N+1 and N-1 layers, which is defined as

$$\Delta(N) = E(N+1) + E(N-1) - 2E(N), \tag{4}$$

where E(N) is the calculated DFT total energy of the fully relaxed N-layer film with the in-plane lattice constant fixed at the theoretical value. The results of both freestanding and supported films are plotted in Fig. 5. A peak in the figure indicates a high relative stability for the film. It is not surprising that the N=5 film is particularly stable as is evident from the discussion above. Comparing the results of the freestanding and supported films, one major effect of the substrate is to completely reverse the situation of the N=2 film, changing it from a highly unstable configuration to a highly stable one. In addition, the peak in  $\Delta(N)$  at N=5 is enhanced by the substrate compared with its neighboring values. Also plotted in Fig. 5 are the experimental annealing temperatures above which the Ag/Fe(100) films of N monolayers start to disintegrate into regions of N+1 and N-1layers.<sup>6</sup> One can see that the values for N=2 and 5 are particularly high, consistent with the features in the calculated  $\Delta(N)$ .

In summary, we have studied the properties of Ag(100) films, up to more than 20 layers, on the Fe(100) substrate by first-principles DFT calculations. This provides an unambiguous and quantitative description of the features of the QW states and the consequent size-dependent stability of the film. A simple quantization model is found to be valid over a wide range of thickness. The phase shift of the electronic wave function at the Ag-vacuum interface is determined as a function of energy, which is numerically different from the result using the WKB approximation. The energy-dependent



FIG. 5. The second difference of the total energy as a function of thickness for freestanding (upper panel) and supported (middle panel) Ag films, in comparison with the experimental annealing temperature (lower panel) at which the film of N monolayers disintegrates into regions of N+1 and N-1 layers (Ref. 6).

phase shift at the film-substrate (Ag-Fe) interface is also deduced from the calculation, which is found to behave quite differently from that of the Ag-vacuum interface. We have calculated the second difference of the total energy, as a measure of relative film stability, for both the freestanding and supported Ag films. It is found that the substrate has a major effect on film stability. The Fe substrate not only enhances the stability of the N=5 film but also gives rise to a new stable thickness of N=2.

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- <sup>1</sup>For a review, see T.-C. Chiang, Surf. Sci. Rep. **39**, 181 (2000).
- <sup>2</sup>M. Hupalo, S. Kremmer, V. Yeh, L. Berbil-Bautista, and M.C. Tringides, Surf. Sci. **493**, 526 (2001); M. Hupalo and M.C. Tringides, Phys. Rev. B **65**, 115406 (2002).
- <sup>3</sup>W.B. Su, S.H. Chang, W.B. Jian, C.S. Chang, L.J. Chen, and T.T. Tsong, Phys. Rev. Lett. 86, 5116 (2001).
- <sup>4</sup>R. Otero, A.L. Vázquez de Parga, and R. Miranda, Phys. Rev. B 66, 115401 (2002).
- <sup>5</sup>H. Hong, C.M. Wei, M.Y. Chou, Z. Wu, L. Basile, H. Chen, M. Holt, and T.-C. Chiang, Phys. Rev. Lett. **90**, 076104 (2003).
- <sup>6</sup>D.-A. Luh, T. Miller, J.J. Paggel, M.Y. Chou, and T.-C. Chiang, Science **292**, 1131 (2001).

- <sup>7</sup>J.J. Paggel, C.M. Wei, M.Y. Chou, D.-A. Luh, T. Miller, and T.-C. Chiang, Phys. Rev. B 66, 233403 (2002).
- <sup>8</sup>H.-R. Tang, W.-N. Wang, and K.-N. Fan, Chem. Phys. Lett. **355**, 410 (2002).
- <sup>9</sup>For a review, see Z.Q. Qiu and N.V. Smith, J. Phys.: Condens. Matter 14, R169 (2002).
- <sup>10</sup>M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
- <sup>11</sup>J.E. Ortega and F.J. Himpsel, Phys. Rev. Lett. **69**, 844 (1992); J.E. Ortega, F.J. Himpsel, G.J. Mankey, and R.F. Willis, Phys. Rev. B **47**, 1540 (1993).
- <sup>12</sup>T. Miller, A. Samsavar, G.E. Franklin, and T.-C. Chiang, Phys. Rev. Lett. **61**, 1404 (1988).
- <sup>13</sup>N.V. Smith, N.B. Brookes, Y. Chang, and P.D. Johnson, Phys. Rev. B 49, 332 (1994).

- <sup>14</sup>S. Crampin, S. De Rossi, and F. Ciccacci, Phys. Rev. B 53, 13 817 (1996).
- <sup>15</sup>G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11 169 (1996), and references therein.
- <sup>16</sup>D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- <sup>17</sup>J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
- <sup>18</sup>J.J. Paggel, T. Miller, and T.-C. Chiang, Science **283**, 1709 (1999); Phys. Rev. B **61**, 1804 (2000).
- <sup>19</sup>P.T. Coleridge and I.M. Templeton, Phys. Rev. B **25**, 7818 (1982).
- <sup>20</sup>S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. 88, 116801 (2002).
- <sup>21</sup>E.G. McRae and M.L. Kane, Surf. Sci. 108, 435 (1981).
- <sup>22</sup>Z. Zhang, Q. Niu, and C.K. Shih, Phys. Rev. Lett. 80, 5381 (1998).