Stress, strain, and charge transfer in Ag/Pt(111): A test of continuum elasticity theory

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We study the validity of continuum elasticity theory for the heteroepitaxial Ag/Pt(111) system, by performing *ab initio* calculations of the structure, stress, and elastic constants. Interlayer separations after the deposition of about 3 monolayers of Ag are close to those predicted by continuum elasticity theory. The surface stress is slightly greater than that predicted by continuum elasticity theory, due to a small charge transfer of about 0.05 electrons from the first Ag layer to the first Pt layer. The deposition of subsequent Ag layers does not affect the charge distribution materially. Our results disagree with a previous finding that the surface stress is larger than that predicted by continuum elasticity theory by an order of magnitude.

I. INTRODUCTION

In the area of thin-film technology, one of the major goals is the ability to grow epitaxial layers in a controlled fashion. When overlayers of a material are deposited on a flat substrate, three kinds of growth modes are possible. In Frank-Van der Merwe growth, the growth proceeds in a layer-by-layer fashion, whereas in Volmer-Weber growth, the overlayer clumps up into three-dimensional islands. In between these two growth modes is Stranski-Krastanov growth, where initial layers are laid down layer by layer, but subsequent deposition results in the formation of three-dimensional islands.

For technological applications (such as the manufacture of devices where the integrity of the interface is crucial), it is desirable to have layer-by-layer growth, with no clumping or fracture of the overlayer. One therefore needs to arrive at an understanding of the factors controlling the growth mode. Some general guidelines to favor controlled layer-by-layer epitaxy are known. It is desirable that the surface energy of the overlayer material be lower than that of the substrate. Further, the misfit between the natural lattice constants of the overlayer and the substrate should be small. If this is the case, then one assumes that the accumulated stress that builds up with the deposition of successive overlayers is also small, thus permitting the growth of dislocation-free epitaxial layers.

This assumption that small misfits lead to small stresses (as predicted by continuum elasticity theory) was, however, called into question in a paper by Grossmann *et al.*[1] who performed cantilever bending experiments to deduce the induced stress when layers of Ag were deposited on a Pt(111) substrate. They obtained the astonishing result that the measured surface stress was greater than that predicted by continuum elasticity theory by an order of magnitude. Subsequently, after correcting some details of their analysis, this enhancement in surface stress was scaled down to a factor of 5.[2] However, this is still a large factor. If this huge discrepancy between the predicted and actual stress indeed exists, it is worrisome for the crystal grower, since one has to rethink the fundamental assumptions made concerning how to favor layer-by-layer growth—which would now become hard to achieve even with small misfits. In their paper, Grossmann

et al. postulated that the discrepancy between the predicted and measured values of surface stress might be due to a large charge transfer (of about 0.43 electrons per atom) from the silver film to the platinum substrate, due to the lower electronegativity of Ag compared to Pt.

However, the validity of the results of Grossmann *et al.* has been questioned by Bottomley,[3] who reexamined the cantilever bending experiments and raised doubts about the assumptions made in deriving the surface stress from the amount of bending.

In this paper, I attempt to resolve this issue by performing *ab initio* density-functional theory calculations to compute the surface stress of the Ag/Pt(111) system. It is shown below that while the stress is indeed larger than predicted by continuum elasticity theory, this discrepancy is considerably smaller than that reported by Grossmann *et al.*

While I am not aware of any technological applications that directly involve Ag-Pt interfaces, the Ag/Pt(111) system has become one of the canonical model systems used to obtain an understanding of the factors controlling growth, and has been the subject of a number of previous experimental and theoretical investigations. Many of these concern the diffusion of individual Ag atoms or small clusters of Ag atoms in this system, and need not concern us here. Of some relevance to this work, however, is the work of Roeder *et al.*,[4] who found, using scanning tunneling microscopy, that for submonolayer coverages of Ag, there is a monolayer-confined intermixing of Ag and Pt. However, upon depositing 1 monolayer (ML) of Ag, there is a demixing of the two metals, and a complete monatomic Ag layer is formed. Subsequently, Brune *et al.* found (again using scanning tunneling microscopy) that while the first Ag layer grows pseudomorphically, the deposition of a second Ag layer results in the formation of a network of misfit dislocations, with alternating domains of face-centered-cubic and hexagonal-close-packed stacking at the surface.[5]

II. *AB INITIO* CALCULATIONS

The *ab initio* calculations were performed using the "PWSCF" package,[6] within the framework of density-functional theory. Both Ag and Pt atoms were treated using an ultrasoft pseudopotential.[7] A plane-wave basis set with a

cutoff of 20 Ry was employed; the cutoff was increased to 160 Ry for expanding the augmentation charges associated with the use of the ultrasoft pseudopotential. Electron-electron interactions were described within the local density approximation (LDA) to the exchange-correlation functional. For bulk systems, two different unit cells were used: (i) a primitive fcc unit cell, with k-point sampling corresponding to 60 points in the irreducible Brillouin zone (IBZ) and (ii) a cell with three layers stacked along the [111] direction, and 69 k points in the IBZ. It was verified that for the unstrained case, the two unit cells gave essentially the same result. Surface calculations were performed for nine or more layers stacked along the [111] direction, separated by a vacuum of thickness equivalent to seven layers, using a $15 \times 15 \times 1$ wave vector grid, corresponding to 27 k points in the surface IBZ. For the clean surface calculations, the three innermost layers were fixed at the bulk separation, and the three outermost layers on either side were allowed to relax. For calculations on the heteroepitaxial Ag/Pt(111) system, one to seven layers of Ag were adsorbed on both sides of a seven-layer Pt slab. The three Pt layers at the center of the slab were fixed at the bulk separation; all other layers were permitted to relax. *Ab initio* stresses were obtained not from numerical derivatives of the total energy but directly, making use of the stress theorem of Nielsen and Martin.[8]

III. RESULTS FOR BULK Pt AND Pt(111)

The lattice constant for bulk Pt is determined to be 3.92 Å, which is in excellent agreement with experiment. This means that the in-plane lattice constant for Pt(111) is $a_\parallel^0 = 2.768$ Å, and successive layers along the [111] direction are separated by $a_\perp^0 = 2.260$ Å. For the clean Pt(111) surface, the expansion/contraction of the three outermost interlayer spacings is found to be $\Delta_{12} = 0.29\%$, $\Delta_{23} = -0.55\%$, and $\Delta_{34} = -0.18\%$, corresponding to very small relaxations of 0.007, -0.012 and -0.004 Å, respectively. These results agree well with previous calculations and experimental data.[9–12] The surface energy and surface stress are found to be 0.124 and 0.400 eV/Å², respectively, again in good agreement with previously published results.[9,10,13]

IV. RESULTS FOR BULK Ag AND Ag(111)

The lattice constant for bulk Ag is found to be 4.02 Å, which is smaller than the experimental lattice constant of 4.09 Å by 1.7%, which is typical of errors due to use of the LDA. This means that the interlayer spacing along the [111] direction in bulk Ag is $b_\perp^0 = 2.320$ Å, and the in-plane lattice constant for pure Ag is $b_\parallel^0 = 2.842$ Å.

Since we wish to study the response of Ag layers to strains imposed by the Pt substrate, it is of interest to calculate the elastic constants of bulk Ag. By isotropically varying the volume of the fcc unit cell, and seeing how the total energy varies as a function of the lattice constant, we obtain $C_{11} + 2C_{12} = 3.99 \times 10^{11}$ N/m², which is larger than the experimental value[14] of 3.1×10^{11} N/m². Similarly, from the change in total energy upon stretching the cell along the body diagonal, we obtain $C_{11} + 2C_{12} + 4C_{44} = 6.7$

TABLE I. Stresses and strains for bulk Ag, strained in the $x'y'$ plane, as obtained from *ab initio* calculations and continuum elasticity theory. The latter uses the formulas of continuum elasticity theory but *ab initio* values of the elastic constants. $b_\perp$ is the distance between successive layers stacked along $z' = [111]$ and $\sigma_\parallel$ is the stress component $\sigma_{x'x'}$.

Strain	Quantity	From *ab initio*	From continuum elasticity
2.6%	$b_\perp$	2.37 Å	2.37 Å
2.6%	$\sigma_\parallel$	0.61×10^{10} N/m²	0.63×10^{10} N/m²
4.2%	$b_\perp$	2.41 Å	2.40 Å
4.2%	$\sigma_\parallel$	1.18×10^{10} N/m²	1.02×10^{10} N/m²

$\times 10^{11}$ N/m², which is again larger than the experimental value[14] of 4.9×10^{11} N/m². This significant stiffening in the theoretical values of C_{11}, C_{12}, and C_{44} presumably arises primarily from overbinding due to the use of the local-density approximation, and will have to be accounted for when we later examine values for stresses.

Another factor that has to be accounted for is the fact that our *ab initio* calculations get exactly the right value for the lattice constant of Pt, but underestimate the lattice constant of Ag. (This presumably arises from the differing quality of the pseudopotentials used for the two elements. The slight overbinding obtained for Ag is a typical LDA error; in the case of Pt, this effect appears to be canceled by the pseudopotential used.) This means that, if we were to perform calculations for Ag layers deposited on an unstrained Pt substrate, we would be underestimating the strain—the strain for the experimental system is 4.2%, whereas the strain in the theoretical system would be only 2.6%. Underestimating the strain would also lead, obviously, to underestimating the induced stresses, which are the quantities that we are primarily interested in. To deal with this problem, we will consider two kinds of epitaxy (i) Ag deposited on unstrained Pt(111), with $a_\parallel = b_\parallel = 2.768$ Å, corresponding to an in-plane strain $\epsilon_\parallel = (b_\parallel^0 - a_\parallel)/b_\parallel^0$ of 2.6%, (ii) Ag deposited on strained Pt(111), with $a_\parallel = b_\parallel = 2.722$ Å, corresponding to $\epsilon_\parallel = 4.2\%$.

Before going on to study the Ag/Pt(111) system, we investigate the validity of continuum elasticity theory for strains of these magnitudes imposed on bulk Ag. We consider a strained Ag crystal, with layers stacked along $\hat{z}' = [111]$. $b_\parallel$, the in-plane lattice constant [in the $x'y'$ or (111) plane] is fixed and the layers are allowed to relax along z' to find $b_\perp$, the optimal spacing between layers, as predicted by *ab initio* calculations. (The coordinate system is denoted by primes to distinguish it from the conventional cubic coordinate system xyz.)

The value of $b_\perp$ can also be estimated using continuum elasticity theory. Imposing the condition that, in the primed system, there is no stress along $\hat{z}' = [111]$, and transforming back to conventional cubic coordinates, one obtains

$$b_\perp = b_\perp^0 \left[1 + \left(\frac{2C_{11} + 4C_{12} - 4C_{44}}{C_{11} + 2C_{12} + 4C_{44}} \right) \left(\frac{b_\parallel^0 - a_\parallel}{b_\parallel^0} \right) \right]. \quad (1)$$

Table I compares the values for $b_\perp$, as obtained from *ab*

initio calculations and continuum elasticity theory, using the theoretically determined values of $C_{11}+2C_{12}$ and C_{44}. The agreement is found to be good.

We also obtain the in-plane stress $\sigma_\parallel = \sigma_{x'x'} = \sigma_{y'y'}$ from the *ab initio* calculations on the strained Ag crystal. This quantity too can be obtained from continuum elasticity theory, where, for a strain $\epsilon_\parallel$ applied in the (111) plane, one gets

$$\sigma_\parallel = \frac{2\epsilon_\parallel}{3}\left[(C_{11}+2C_{12}+C_{44}) - \frac{(C_{11}+2C_{12}-2C_{44})^2}{(C_{11}+2C_{12}+4C_{44})}\right]. \quad (2)$$

Table I also compares the values for $\sigma_\parallel$ as obtained from *ab initio* calculations and continuum elasticity theory; once again the two approaches are found to give values in good agreement with each other. From this, we may conclude that continuum elasticity theory gives a good description of the properties of bulk Ag, if we account for the overestimation of elastic constants in the *ab initio* calculations. For later application to the case of Ag/Pt(111) heteroepitaxy, we note that the results for $\sigma_\parallel$ (using continuum elasticity theory and the *ab initio* values of elastic constants) imply that each layer of Ag will contribute an amount of 1.49 N/m to the interface stress for the case $\epsilon_\parallel = 2.6\%$, and 2.46 N/m for the case $\epsilon_\parallel = 4.2\%$.

For unstrained Ag(111), the *ab initio* calculations give a surface energy of 0.072 eV/$\mathring{A}^2$. Note that this value is considerably smaller than the corresponding value for Pt(111), which is what makes the Ag/Pt(111) system a promising candidate for layer-by-layer growth. The first three interlayer spacings are very slightly contracted, with $\Delta_{12}=-0.87\%$, $\Delta_{23}=-0.66\%$, and $\Delta_{34}=-0.46\%$. These relaxations are in very good agreement with a recent low-energy electron-diffraction study[15] which found $\Delta_{12}=(0.0\pm0.9\%)$ and $\Delta_{23}=(0.0\pm1.3\%)$, but are somewhat smaller than the values of $\Delta_{12}=-2.5\%$ and $\Delta_{23}=+0.6\%$ obtained from medium energy ion scattering experiments.[16]

V. RESULTS FOR Ag/Pt(111)

In the calculations for Ag/Pt(111), one to seven layers of Ag are "deposited" on both sides of a Pt(111) slab. It is assumed that the deposition is epitaxial and pseudomorphic, with no intermixing. For the reasons mentioned above, two cases are considered (i) $a_\parallel = b_\parallel = 2.768\ \mathring{A}$, and (ii) $a_\parallel = b_\parallel = 2.722\ \mathring{A}$. For this latter case, we first find, from an additional series of *ab initio* calculations on strained bulk Pt, that the optimal interlayer separation for the Pt substrate is $a_\perp = 2.304\ \mathring{A}$. [This is in excellent agreement with the value of 2.305 Å obtained using Eq. (1) and experimental values of the elastic constants of bulk Pt from Ref. 14.] The three interlayer separations at the center of the Pt slab are fixed at this value, all other interlayer separations are relaxed by calculating the energies and forces *ab initio*.

Figures 1 and 2 show the interlayer separations (along [111]) for the two cases of strain considered. For notational convenience, we label Pt layers by Arabic numerals 1, 2, 3, etc., starting with the outermost Pt layer at the interface and
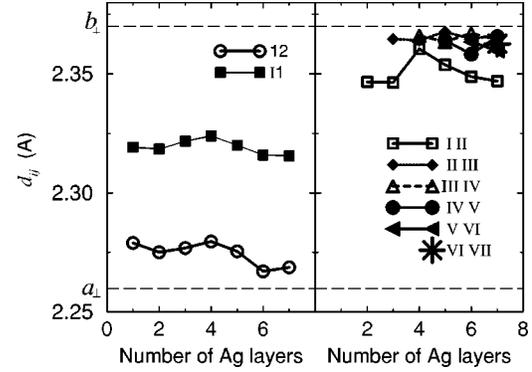
FIG. 1. Variation in interlayer separations d_{ij} in the Ag/Pt(111) system (for the case where the in-plane strain is 2.6%), as a function of the number of Ag overlayers deposited. The numbering convention is explained in the text. $a_\perp$ is the bulk interlayer spacing for the Pt substrate, and $b_\perp$ is the interlayer spacing for bulk Ag strained by this amount.

proceeding inwards, and label successive Ag layers by Roman numerals I, II, III, etc., again starting the numbering at the interface, and proceeding outwards. From Figs. 1 and 2, we see that the interlayer spacings near the interface are fairly sensitive to the number of overlayers deposited, and are bounded by $a_\perp$ and $b_\perp$. (Note that the values of $a_\perp$ and $b_\perp$ are different for Figs. 1 and 2.) The distance between the first two Pt layers at the interface is slightly expanded relative to $a_\perp$; while the distance between the first two Ag layers at the interface is slightly less than $b_\perp$. d_{1I}, the distance between the outermost layer of Pt atoms and the innermost layer of Ag atoms, is roughly midway between $a_\perp$ and $b_\perp$. The variation of subsequent interlayer spacings with the number of Ag overlayers deposited is nonmonotonic; however all distances from $d_{II\ III}$ onwards are close to $b_\perp$. These results are qualitatively similar to those reported for semiconductor interfaces by Brandt *et al.*,[17] who found that a 3 ML film behaves close to an elastic continuum, but the predictions of continuum elasticity theory are significantly off for the limit of a single monolayer.
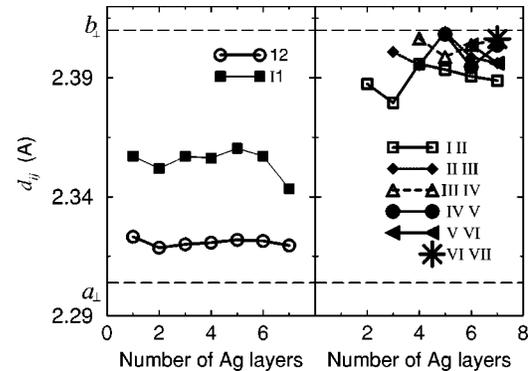
FIG. 2. Variation in interlayer separations d_{ij} in the Ag/Pt(111) system (for the case where the in-plane strain is 4.2%), as a function of the number of Ag overlayers deposited. The numbering convention is explained in the text. $a_\perp$ is the bulk interlayer spacing for the Pt substrate, and $b_\perp$ is the interlayer spacing for bulk Ag strained by this amount.
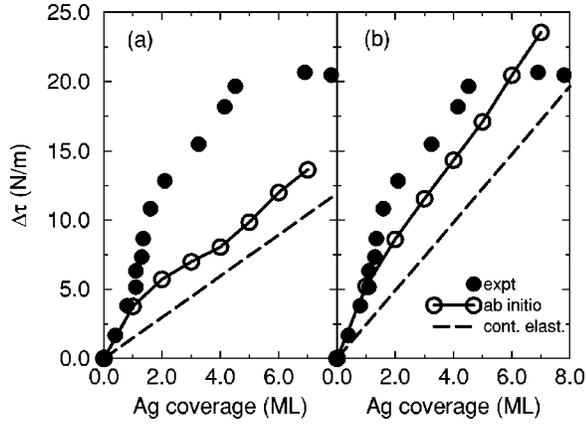
FIG. 3. The induced surface stress $\Delta\tau$ as a function of Ag coverage. The black dots are experimental points from Ref. 1, scaled down by a factor of 2/3 as recommended in Ref. 2. The open circles are *ab initio* results, and the dashed line is the prediction from continuum elasticity theory, using *ab initio* values of elastic constants. The theoretical values in Figs. (a) and (b) are for $\epsilon_\parallel = 2.6\%$ and $\epsilon_\parallel = 4.2\%$, respectively.

FIG. 4. Charge densities integrated over the $x'y'$ plane, as a function of the vertical position z', for (a) 1 ML of Ag deposited on Pt(111), (b) 1 ML of Ag (solid line) and Pt(111) slab (dashed line), (c) induced charge density, obtained by subtracting the two curves in (b) from the curve in (a). The black dots and asterisks indicate the centers of the Pt layers and Ag layer, respectively.

In the *ab initio* calculations, we also compute the stress for the Ag/Pt(111) system. For the case of $\epsilon_\parallel = 2.6\%$, there is no strain on the bulk layers of the Pt substrate, and thus any calculated stress can be attributed to the Ag/Pt(111) interface. However, for the case $\epsilon_\parallel = 4.2\%$, the Pt substrate has also been strained. The corresponding stress in these Pt layers is subtracted out by computing the stress on bulk Pt layers strained in the $x'y'$ plane by this amount. Further, in order to compare with the cantilever bending experiments, which measured the induced stress upon deposition of Ag, we need to subtract out the surface stress of Pt(111).

More precisely, we have carried out the following steps, in order to be able to get quantities that we can compare directly with the experimentally reported values: (a) We take a slab with the requisite number of Ag layers adsorbed on both sides of the Pt slab. For the relaxed slab, we obtain the in-plane stress (force per unit area) for the whole slab. This procedure is carried out for both values of $\epsilon_\parallel$, viz., 2.6% and 4.2%. (b) Only for the case $\epsilon_\parallel = 4.2\%$, we subtract out the stress from bulklike Pt layers, by comparing with the stress of bulk Pt strained by 4.2% in the (111) plane. (c) We integrate the stress along the z' direction to obtain $\tau_1 = \frac{1}{2}\int dz' \sigma_\parallel$, where the factor of $\frac{1}{2}$ arises from the fact that we have two Ag-Pt interfaces in our slab. This quantity can be thought of as representing the surface/interface stress (dimensions of force per unit length), though it is really distributed over many layers. (d) Compute *ab initio* the surface stress τ_2 for clean Pt(111) for both the unstrained Pt substrate (as mentioned above) and for a Pt(111) slab strained by 4.2%. (e) Finally obtain $\Delta\tau = \tau_1 - \tau_2$, which is the induced interface stress, which is the quantity that the experiments try to measure.

Our results for $\Delta\tau$ as a function of Ag coverage are plotted in Figs. 3(a) and 3(b) for $\epsilon_\parallel = 2.6\%$ and 4.2%, respectively. The filled circles in these figures are the experimental points; however, these are approximate, and have been ob-

tained by scaling the data in Ref. 1 by a factor of 2/3, as recommended in Ref. 2. The open circles are the *ab initio* results obtained using the procedure outlined in the preceding paragraph. The dashed lines are the results from continuum elasticity theory, using *not* the experimental values for C_{11}, C_{12}, and C_{44}, but the theoretically determined (*ab initio*) values. While it might appear from Fig. 3(b) that there is good agreement between the experimental and theoretical values, this agreement is somewhat misleading, because of the overestimation of the elastic constants in the calculations. What we can conclude, however, is that the interface stress is indeed larger than predicted by continuum elasticity theory, though not by the huge amount suggested in Refs. 1 and 2.

One point worth noting is that the ratio of the *ab initio* stresses for the two cases $\epsilon_\parallel = 2.6\%$ and $\epsilon_\parallel = 4.2\%$ is more or less equal to the ratio of the values of the strain; giving us additional confidence that the correct procedure was used in subtracting out the stresses in the Pt layers for the case where the Pt substrate is also strained.

Why is the interface stress larger than that calculated from continuum elasticity theory? Grossmann *et al.* suggested that charge transfer from Ag atoms to the more electronegative Pt atoms might be responsible. They estimated a charge transfer of 0.43 electrons per Ag atom. We can check this by comparing the charge distribution for the Ag/Pt(111) system to the separate charge densities of the Ag layers and Pt layers.

In Fig. 4, we plot the charge densities, integrated over the $x'y'$ plane, as a function of z', the coordinate that runs
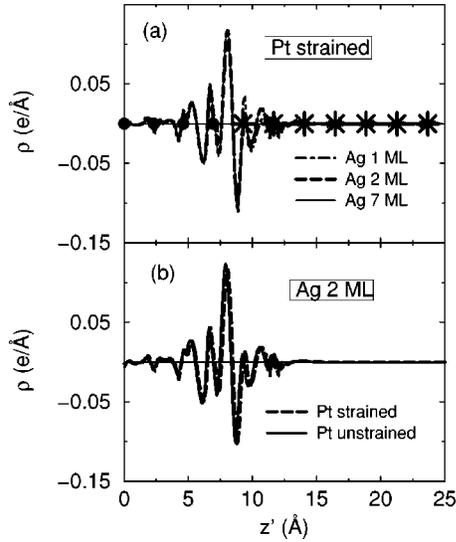
FIG. 5. Induced charge density, integrated over the $x'y'$ plane, as a function of the vertical position z': (a) for Ag coverage ranging from 1–7 ML, with the Pt substrate strained. The black dots and asterisks indicate the centers of the Pt layers and Ag layers, respectively, for the case where the Ag coverage is 7 ML, (b) with the Pt substrate strained and unstrained for Ag coverage of 2 ML.

normal to the interface. The results are shown for the case $\epsilon_\parallel = 4.2\%$. Figure 4(a) shows the charge density for the Ag/Pt(111) system, with one layer of Ag deposited on the Pt substrate. Figure 4(b) shows the separate charge densities for a single Ag layer (solid line) and a slab of Pt atoms (dashed line). Figure 4(c) shows the charge-density distribution induced by the deposition of an Ag layer on a Pt substrate. This is obtained by summing the two curves in Fig. 4(b) and then subtracting the curve in Fig. 4(a). From Fig. 4(c), we find that the charge transfer from Ag to Pt is small (about 0.05 electrons) and that the charge distribution along z' is highly nonuniform. The induced charge density is localized primarily in the region of the interface, with a depletion in charge close to the Ag layer and a build up close to the first Pt layer. There is also a smaller but still pronounced redistribution of charge density between the first and second Pt layers.

How does this induced charge density change as additional layers of Ag atoms are deposited? These results are shown in Fig. 5(a). The most notable feature is that the induced charge density is more or less independent of the number of Ag overlayers. There is a very slight change on going from a coverage of 1–2 ML; after that, up to 7 ML, there is no perceptible change [for clarity, only the results for 1, 2, and 7 ML are plotted in Fig. 5(a); the results for 3–6 ML are essentially indistinguishable from those for 2 and 7 ML]. This suggests that charge is donated to the Pt substrate only by the first layer of Ag atoms at the interface. Note also that there is a slight redistribution of charge between the first and second Ag layers. It should be noted that to obtain the induced charge densities plotted in this figure, in all cases the charge density for the isolated Pt(111) slab was obtained using *not* the coordinates for a relaxed Pt(111) slab, but that corresponding to a Pt slab whose layers were in the same positions as those for the relaxed Ag/Pt(111) slab; i.e., the
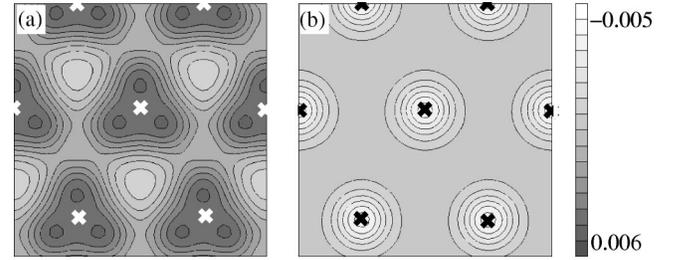
redistribution of charge in this figure arises entirely from charge transfer due to the presence of the interface, and not due to changes in interlayer spacings upon deposition of overlayers.

Figure 5(b) shows that the induced charge distribution is relatively insensitive to the strain we have imposed on the substrate, by comparing the results obtained with a strained and unstrained Pt substrate, for a coverage of 2 ML of Ag. The two curves are almost identical, except for a very slight lateral shift (along z') due to the outward expansion of the Pt substrate in the strained case.

In order to estimate the excess surface stress due to this charge transfer, we need to consider the distribution of induced charge in the $x'y'$ plane. This is shown in the shaded contour plots of Fig. 6 for two cuts perpendicular to the z' axis. Figure 6(a) shows the induced charge density for the plane $z' = 8.0$ Å, which lies between the outermost layer of Pt atoms and the innermost layer of Ag atoms. (The reason for picking this plane is that this is where the induced positive charge density is largely localized, as can be seen from Fig. 5.) The white crosses show the projection of the positions of the outermost layer of Pt atoms, which are centered a distance 1.08 Å below this plane. An anisotropically distributed positive charge density is seen to be induced in this plane, localized primarily in the neighborhood of the outermost layer of Pt atoms. Figure 6(b) also shows the induced charge density, but for the plane $z' = 5.83$ Å. The planes in Figs. 6(a) and 6(b) are equidistant from the outermost layer of Pt atoms, but the former lies above it (towards the Ag layers) and the latter lies below it (away from the Ag layers). A comparison of the two figures shows that the sign, magnitude, and distribution of the induced charge is quite different in the two cases, underlining the influence of the Ag overlayers.

To estimate the contribution of this charge transfer to the surface stress, we use a simple model of a parallel-plate capacitor, following Ref. 1. The contribution $\Delta\tau_q$ to the surface stress is given by

FIG. 6. Induced charge density for the Ag/Pt(111) system for the planes (a) $z' = 8.0$ Å and (b) $z' = 5.83$ Å. The white crosses in (a) and the black crosses in (b) mark the projections onto the plane of the centers of the outermost layer of Pt atoms. The gray scale runs from -0.005 to 0.006 in atomic units (electrons/bohr^3).

$$\Delta\tau_q = -\frac{(\Delta q)^2 d_{eff}}{2\epsilon_0 A^2},\qquad(3)$$

where Δq is the charge transferred, d_{eff} is the spacing between the positive and negative charge, ϵ_0 is the permittivity

constant, and A is the area over which the charge is distributed. Taking $\Delta q = 0.05$ electrons, d_{eff} [obtained from Fig. 5(a)] as 0.78 Å, and A [estimated from Fig. 6(a)] as 1 Å^2, this back-of-the-envelope calculation gives $\Delta \tau_q = 2.8$ N/m, which is indeed roughly equal to the difference, in Fig. 3(b), between the *ab initio* and continuum elasticity theory values for the surface stress $\Delta \tau$.

VI. DISCUSSION AND SUMMARY

The results presented in the preceding section differ considerably from the interpretations and intuitive assumptions of Grossmann *et al.*[1] We consider the differences one by one: (i) They assumed that charge was homogeneously depleted from the first few monolayers of the Ag film, whereas we find that charge is essentially depleted from only the very first layer of Ag atoms. (ii) They assumed that the countercharge sits in the first layer of Pt atoms, whereas we find it is localized between the Ag and Pt layers. (iii) They assumed that as additional Ag layers are deposited, more and more charge is transferred from Ag to Pt layers, whereas we find that the induced charge density saturates after the deposition of the first Ag layer. (iv) Due to the preceding assumptions, in their case, the induced surface stress due to charge transfer would vary linearly with the thickness of the Ag film, whereas we find that this quantity is roughly independent of the Ag coverage. This is in agreement with our results shown in Fig. 3, where the total surface stress (which includes contributions from strained Ag layers and charge transfer) is found to differ from the stress estimated by continuum elasticity theory (which includes only the contribution from the strained Ag layers) by an amount that is more or less independent of the number of Ag layers. (v) By comparing with their experimental results, and making use of the assumptions cited above, they estimated a charge transfer of 0.43 electrons per Ag atom. However, we obtain a much smaller charge transfer of approximately 0.05 electrons, independent of the number of Ag overlayers.

Possible sources of errors in our calculations are the use of the local density approximation, and the use of a pseudopotential. We have learned recently that two other groups have also been investigating the same system, using different techniques: in one case a mixed basis calculation, and in the other all-electron linearized augmented plane-wave calculations.[18,19] When their results become available, it would be interesting to compare our results with theirs, thus nailing down, for example, possible errors due to the use of a pseudopotential.

One further caveat should be mentioned: as stated above, we have assumed that the Ag layers are grown pseudomorphically on the Pt substrate. However, experiments have shown that, upon annealing a film deposited at room temperature, the structure of the bilayer consists of a network of misfit dislocations.[5] Since these misfit dislocations serve to relieve surface stress, we can consider our *ab initio* numbers for surface stress to be an upper limit. However, the experimental results that we have plotted in Fig. 3 were obtained at 300 K, so our comparison remains valid. Also, since in this work we have confined ourselves to integral coverage, we need not worry about the finding of Roeder *et al.*[4] that a surface alloy is formed for fractional coverage.

To summarize our main results: We find that continuum elasticity theory provides a good description of the properties of bulk Ag, if we allow for the overestimation of elastic constants arising from overbinding due to the use of the local-density approximation for the exchange-correlation functional. For the Ag/Pt(111) system, we find that interlayer relaxations are nonmonotonic and sensitive to the number of Ag overlayers. The interlayer spacings are close to those predicted by continuum elasticity theory after the deposition of about 3 ML of Ag. The surface stress is slightly larger than that predicted by continuum elasticity theory (again allowing for the overestimation of the elastic constants), and this difference can be attributed to charge transfer from the innermost layer of Ag atoms to the outermost layer of Pt atoms. However, the amount of this charge transfer, and the resulting enhancement in surface stress, is considerably smaller than that reported in the experiment of Grossmann *et al.*[1] This discrepancy may be due to some intuitive assumptions made in the analysis of this experiment, which have subsequently been questioned.[3] Other differences between the assumptions made in Ref. 1 and our results have been listed at the beginning of this section. We find no evidence for a catastrophic failure of the classical rules of heteroepitaxy, which is reassuring.

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