Revisiting the surface properties of Mg(0001) thin films and their effect on the adatom binding energy and self-diffusion

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Abstract

We perform first-principles calculations of the properties of the Mg(0001) surface of thin films to examine the giant oscillations of surface energy and interlayer relaxation of Mg(0001) films as a function of thickness reported previously. We find that, although overcoming the *thin-film limit* requires up to 25 layers, properties exclusive to the surface layer are well converged for 18-layer thick films (~4.1 nm). Furthermore, the fcc-stacking fault is found to be energetically favorable for the Mg adatom by 15 meV. We also find that the binding energy of the Mg adatom (~0.6 eV), well converged for 7-layer films, is significantly weaker than the value reported by previous calculations. In addition, our calculations show small diffusion barrier of 9 meV (hcp to fcc) and 25 meV (fcc to hcp) for the monomer.

Keywords: Magnesium, quantum-size effects, adatom binding energy, stacking fault, adatom self-diffusion.

I. Introduction

The relatively high density of nearly-free electronic states around the Fermi level of materials such as bulk Mg translate into singular properties near a surface or interface, as well as in the thin-film regime, at which quantum size effects may play a role [1-7]. In one such aspect, Schulte predicted oscillations in the work function of films as a function of their thickness [1]. Feibelman later on demonstrated that such oscillations should be palliated because the interlayer spacing is very close to $\lambda_F/2$, where λ_F is the Fermi wavelength [2]. Later calculations by Staikov and Rahman found good convergence for the interlayer relaxation at 13 layers [8]. Wachowicz and Kiejna [3,4] reiterated that quantum-size effects are not of consequence for the surface properties when analyzing the interlayer relaxation, surface energy and work function for film thickness from 3 to 13 layers [3,4]. More recently, however, Li et al. reported calculations predicting large surface-energy, interlayer-relaxation and work-function oscillations as a function of the number of layers. Li et al. found that the surface energy oscillates with the thin-film number of layers with a period of $\Delta N \sim 8$, where N is the number of layers [9]. They found that the oscillations arise from occupation of electronic states close to the Fermi level, even though the oscillation patterns are not as clear as one would expect. The authors ascribed this inconsistency to the fact that the atomic arrangement in the slabs was fully relaxed during the calculations, which makes the ratio between the interlayer spacing and Fermi wavelength to vary throughout the slab and thus breaks the periodicity of the oscillations that otherwise would be obtained for a bulk-terminated slab. They also found a quantum size effect in the interlayer relaxation and suggested 30 monolayers (ML) as semi-infinite surface limit.

The oscillatory behavior of the properties of Mg films as a function of thickness is of fundamental relevance to understanding nearly free-electron-like materials and possibly to understand the growth of Mg films on a substrate. It is also significant in the light of (1) experimental works reporting oxidation-rate thickness dependence [5-7], (2) thickness-dependence of hydrogen-binding-energy [9].

It is surprising that the calculations of Li et al., performed with state-of-the-art methods, render such giant oscillations in the properties of Mg thin films, while earlier calculations have found that 11 – 13 layer are sufficient to characterize the Mg(0001) surface [3,4,8]. Still, nobody but Li

et al. has performed convergence tests for more than 13 layers. One could thus argue that in previous works the studied slabs were not sufficiently thick as to notice the periodic oscillations observed by Li et al.

Magnesium is a nearly-free-electron-like material. The bonding among Mg atoms in the bulk is mainly metallic through the two atomic 3s outer electrons since the 2p electrons screen the ion's charge and thus the $3s^{2-x}3p^x$ bulk states are not tightly bound. The 2p shell is strongly bound and thus barely participates in the bond. Nevertheless, it is well known that the 2p-semicore and the 3s-valence states of magnesium are not entirely independent and thus the former indirectly influence the properties of Mg.

To our knowledge, a study of the level as that in Ref.[9] has not been performed taking into consideration 2p-states, and Li et al. [9] do not specify that information. Thus further testing on their findings is in order. In this work, we present results of a first-principles investigation of the structure and surface energy of Mg(0001) free standing films, as well as of the adsorption site, binding energy and diffusion barrier of Mg adatoms to revise earlier predictions and investigate whether there is evidence that the predicted size effects may affect also the initial stages of epitaxial growth. We shall see that our calculations do not confirm the strong variations of the first-layer expansion and periodic oscillations of surface energy as a function of film thickness reported by Li et al. [9]. On the one hand, we find that the properties exclusive to the surface layer are well converged for 18-layer thick films (~ 4.1 nm). On the other hand, the binding-energy of a Mg adatom and its diffusion barrier are well-converged at 7 layers. The manuscript is organized as follows: In Section II we summarize our computational methodology. In Section III we present our results and discussion. Finally, in Section IV we outline our conclusions.

II. Computational details

We perform periodic density-functional-theory calculations of the total energy the systems of interest. One of the focus of this work is to verify the existence of the giant oscillation reported by Li et al. [9] We thus perform as accurate a calculation, as feasible, of the properties analyzed in Ref.[9] using the same potential type and parameterization for the exchange-correlation

functional. Namely, the interaction between ions and electrons is described by an ultra-soft Vanderbilt pseudo-potential [11] that includes 2p-semicore states (i.e., for atomic Mg, the core electrons and those treated explicitly are as follows: $[\text{core}]^4 2p^6 3s^{2-x} 3p^x$). Moreover, for the electron exchange-correlation functional, we use the parameterization of Perdew and Wang 91 (PW91) based on the generalized gradient approximation (GGA) [12]. These calculations --- implemented in the computational code QUANTUM ESPRESSO [10] --- will be referred as US-PW91-QE calculations.

The rest of the parameters are chosen to obtain convergence up to the third digit in the lattice parameters and cohesive energy. These requirements are more stringent than those reported in the literature, but guarantee convergent results that confidently characterize the outcome of the ultra-soft pseudo-potential with the PW91 parameterization. Specifically, the electronic wave functions are expanded in a plane-wave basis set with a kinetic energy cut-off of 476 eV. The charge density Fourier expansion is truncated at 5440 eV. The Mg(0001) surface is modeled by slabs of thickness from 2 to 30 layers with a 1x1 in plane periodicity. For modeling Mg self-diffusion, convergence tests over the number of layers were performed using an in-plane periodicity of 3x3 atoms for 5, 7 and 9 layers. For integrations inside the Brillouin zone, the latter is sampled according to the Monkhorst–Pack scheme [13] with a uniform grid of k-points of dimensions 16x16x8, 16x16x1, and 5x5x1 for the bulk, the 1x1 surface, and the 3x3 surface, respectively. Integrations use the Gaussian broadening technique for the level occupation with a smearing parameter of 0.1 eV, which is equal to that used in Ref.9 (We find a negligibly dependence of the total energy on the smearing as this varies from 0.05 eV to 0.2 eV in bulk calculations).

In all calculations involving a surface, a vacuum space of 20 Å separated the periodic images of the slab to avoid interaction between them. The positions of all atoms in the slab were optimized until the Hellmann–Feynman forces on each atom and each direction was smaller than $2.57 \times 10^{-3} \text{ eV/\AA}$. The surface energy is calculated as one half of the total energy difference between the n-layer slab and the bulk with the same number of atoms. The factor 1/2 accounts for the two surfaces of the slab.

To rule out that a more accurate treatment of core electrons and a better exchange-correlation functional (better in the sense that it yields bulk lattice parameters and cohesive energy closer to experiment than previous LDA and GGA-PW calculations, as we shall see) do not yield results that are drastically different from those obtained with the PW ultra-soft pseudo-potentials, we compare some of our US-PW91-QE results with those obtained when the valence electronic wave functions are kept orthogonal to the core states [14] and the exchange-correlation parameterization of Perdew-Burke-Ernzerhof (PBE) [15] is used. We have applied the former condition by using the projected-augmented-wave-method (PAW) pseudo-potential [14], as implemented in the Vienna Ab-initio Simulation Package (VASP) [16]. Thus, we shall refer to these calculations as the PAW-PBE-VASP calculations. In these, 2p-semicore states are also included. The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off of 265.6 eV. The Mg(0001) surface was modeled by 3-30 layers with a 1x1 in plane periodicity. For modeling Mg adatoms on Mg(0001), the number of layers for the supercell was fixed to 7 and the in-plane periodicity was 3x3. For the integrations inside the Brillouin zone, the latter was sampled according to the Monkhorst–Pack scheme [13] with uniform grid of k-points of dimensions 16x16x8, 16x16x1, and 5x5x1 for the bulk, the 1x1 surface, and the 3x3 surface, respectively. The integrations use the Gaussian broadening technique for the level occupation with a smearing parameter of 0.10 eV. In all calculations involving a surface a vacuum space of 20 Å separated the periodic images of the slab to avoid interaction between them. Minimization of the total energy of the slab as a function of atomic positions is achieved by reducing the Hellmann–Feynman forces on the atoms below 4×10^{-3} eV/ Å via the conjugated gradient algorithm.

Finally, the diffusion barriers of the Mg monomers on Mg(0001) are determined by the dragging method: The total energy of the system at several points along the chosen diffusion path --- which in this case through the bridge sites --- is determined while fixing the coordinate of the Cu adatom along such path and allowing its other coordinates and those of all other atoms in the system to relax.

III. Results and Discussion

1. Properties of bulk Mg

The primitive unit cell of hcp crystals is a hexagonal supercell containing two atoms. Our corresponding US-PW91-QE calculations for bulk Mg yield lattice parameters ($a = 3.213 \text{ \AA}$ and $c/a = 1.607$) and cohesive energy values (1.45 eV) in very good agreement with the experimental values ($a = 3.21 \text{ \AA}$ and $c/a = 1.624$, $E_{\text{coh}} = 1.46 \text{ eV}$) [17] and with the previous calculations [3,4,8,18,19], as shown in Table 1.

Since the c/a -ratio of Mg is approximately constant for varying pressure [20], we have calculated its bulk modulus based on the equilibrium c/a -ratio. Our result, 35.48 GPa, is in excellent agreement with early measurements (35.4 GPa) [21] but slightly underestimates the value obtained in more recent measurements ($36.8 \pm 3 \text{ GPa}$) [20].

For the lattice parameter, results similar to those reported above were obtained in our PAW-PBE-VASP calculations. For bulk Mg, they render the following lattice parameter: $a = 3.195 \text{ \AA}$ and $c/a = 1.62$, both also in good agreement with experiment and previous calculations, particularly with regards to the parameter that is directly related to the interlayer distance, c . Moreover, the PAW-PBE-VASP calculations yield a cohesive of 1.50 eV also in better agreement with experiment than the US-PW91-QE result.

It is worth noticing that our US-PW91-QE calculations yield a cohesive energy 50 meV smaller than that found in previous calculations that also used an ultra-soft pseudo-potential and the PW91 exchange-correlation parameterization (See Table I). Although it is not an alarming discrepancy, it calls our attention because we have made an exhaustive search of the lowest energy lattice parameters (a and c) for both types of calculations (PAW-PBE-VASP and US-PW91-QE) and, as mentioned before, our parameters are chosen to obtain more accurate results than those obtained in Refs.[4] and [9]. Clearly, our data are insufficient and in fact not intended to discern the reason for the differences in the computed cohesive energy. Moreover, while in Ref.[4] it is indirectly indicated that only valence electrons are treated explicitly, whether or not semi-core states are taken into account is not at all clear in Ref.[9]; they only mention that denser k -point meshes do not change the lattice parameter (though that may not hold for the total energy). Still, the fact that the value obtained in Refs.[4] and [9] is the same might indicate that their agreement with experiment is produced by an error cancellation between neglecting the participation of semi-core electrons in the bonding and the PW parameterization, rather than

from the slightly lower accuracy of their calculations with respect to ours, with regards to the number of k-points or the plane waves energy cutoff --- computational differences that are expected to yield smaller total energy differences. On the other hand, once the PAW-PBE pseudo-potential is used, we get indeed a cohesive energy of 1.50 eV, in agreement with Refs.[4] and [9] --- whose results, again, may be coincidental --- and, most importantly, with experiment. This thus indicates us that the proper orthogonalization of the valence wave-function with respect to the core ones, and the PBE functional --- well-known for outperforming PW for most materials --- allow a better simulation of Mg-Mg interaction, and we shall confirm this asseveration in the following subsection.

2. Properties of Mg(0001): The thin-film limit, formation energy, surface energy, interlayer relaxation

In the following we will analyze how the properties of Mg(0001) films vary as a function of the film thickness and find convergent values characterizing such properties. Specifically, we look at (1) the thickness at which the interlayer distance among central layers recovers the bulk value, (2) the formation energy of the film, (3) the surface energy and (4) the interlayer contraction/expansion of topmost layers. All presented results are from our US-PW91-QE calculation unless indicated otherwise.

As we shall see, in this section it will be important to distinguish between the film thickness at which the properties of the surface (the topmost layer) are reliably obtained and the film thickness at which central layers recover the bulk properties: the *thin-film limit*. The two concepts are often equivalent but the long-range charge density Friedel oscillations inside the Mg films will prove that they are not necessarily the same.

First, we have determined the thickness at which the central layers of the film recover the bulk properties, *the thin-film limit*. For example, we find that, in order that the interlayer relaxation at central layers falls below $\pm 0.1\%$ (a value taken as a convergence parameter because it corresponds to the resolution of available LEED experiments [22]), the film must be at least 23 layers thick, although Δd_{34} has been found to be vanishingly small in previous calculations [3,4,8]. For the sake of brevity, we report here only the interlayer relaxation data of the 23-layer

film in Table 2. These results are compared against calculations obtained in our PAW-PBE-VASP calculations.

We have then recalculated the properties reported by Li et al. [9] in order to explicitly test the striking thickness dependence found in their work. Specifically, we have obtained well-converged values of (a) the formation energy per atom, (b) the surface energy, σ , and (c) the relaxation of the first interlayer spacing of Mg(0001), Δd_{12} . These quantities are extracted from our US-PW91-QE calculations and are plotted in Figures 1(a)-(c) for $N = \{2, 30\}$, together with the corresponding results of Li et al. [9] for comparison. Regarding the formation energy per atom (Fig.1(a)), which is also an indicator of the thin-film limit, in agreement with the results in [9], we find that it slowly and monotonically converges to the cohesive energy of bulk Mg, $E_{\text{coh}} = 1.45$ eV/atom. For example, for a film of 17 layers the formation energy is 75 meV/atom lower than E_{coh} , while for a film of 23 layers it is only 15 meV/atom lower than E_{coh} .

Once we have then obtained the above indicator of the *thin-film limit* (around or more than 23 layers), we proceed to determine the thickness at which surface properties converge (the surface energy and the topmost interlayer relaxation). One might think that since a large number of layers are needed to recover the bulk interlayer distance, the conclusions of Li et al. that the surface properties may need more than 30 layers to converge are further confirmed. Nevertheless, we shall see that this is not the case.

Fig. 1(b) evidences that the behavior of the surface energy σ as a function of thickness is indeed not monotonic – it may vary by as much as 7 meV/atom; but only for films of 3 -- 7 layers. However, σ is not periodically oscillatory whatsoever. It actually converges to a value of 0.286 eV/atom, which is in excellent agreement with the experimental value, 0.28 eV/atom [23], within an accuracy of 2 meV/atom for films composed of only 18 layers (corresponding to films thicker than 4.1 nm). This result thus opposes that of Li et al., who reported that the surface energy of thin films oscillates with a relatively long period of $\Delta N \sim 8$ but actually does not but converge even at 30 layers (0.322 eV/atom). Specifically, in their calculations the surface energy has increments of more than 10 meV for films of less than 10 layers and almost steadily increases from 0.307 eV/atom to 0.334 eV/atom as the number of layers increases from 14 to 24 [9], a

value 50% larger than the experimental one. In addition, note that while the formation energy, which is an indicator of the thin-film limit, varies by several meV beyond 24 layers, the corresponding variation of σ – a surface property -- are almost 10 times smaller; suggesting that the properties of the surface converge more rapidly than the properties of the bulk.

In addition, our Fig. 1(c) shows that the dependence of the outward interlayer relaxation Δd_{12} on the thickness of the film is not as dramatic as suggested by the calculations of Li et al. [9]. Namely, although Δd_{12} varies from +3.23% to +1.70% when increasing the number of layers N from 3 to 8, it is already reasonably well described by 11 layers, and totally converged at 17 layers. The converged value of Δd_{12} is 2.20%, which is in good agreement with the experimental value [22], $+1.9 \pm 0.3\%$. The results for the outward relaxation of Mg(0001) are thus again in contrast with those of Li et al.: They found a surprisingly large interlayer expansion of +7% for 3 layers and a converged value of $\sim 0.7\%$, which is an extremely small compared to the experimental value abovementioned. They found also that 20 layers are necessary to obtain convergent values for this surface property because of a strong periodic oscillation of period $\Delta N \sim 8$ for films of thickness ranging from 3 to 19 layers. Regarding the oscillations in Δd_{12} of period $\Delta N \sim 8$, our calculations barely catch that Δd_{12} has local minima at 14-15, 23-24 layer and local maxima at 11, 19 and 27 that might be interpreted as the reported oscillations, however, not only are the deviations of these “extremes” negligible but also films of intermediate thickness fall out from any oscillatory pattern. Moreover, maxima of Δd_{12} in Li et al. calculations correspond to minima in our calculations and vice versa.

We do not know what caused the dramatic thickness dependence of the properties of Mg(0001) obtained in the DFT calculations by Li et al., since the computational methods of the present calculation do not differ from theirs, except in that they used an ultrasoft pseudopotential presumably without semicore p-electrons [9]. However, the large discrepancies of our results with those Li et al. and, more importantly, the poor agreement of their results with available measurements cannot be ascribed to whether or not semicore 2p-state are taken into consideration. Also, based on previous studies (with the same [4] or even fewer k-points [8] and plane waves [8]), one can assume that the computational parameters reported by Li et al. are reliable. Our goal here was to either confirm or refute the presence of the oscillations rather than

try to reproduce the results of Ref.[9]. Moreover, our (US-PW91-QE) results for the interlayer relaxations are in general confirmed by our PAW-PBE-VASP calculations. Namely, in going from the ultra-soft PW91 pseudo-potential to the PAW-PBE one, there are no differences suggesting that our US-PW91-QE calculations simply fail to reproduce either the strong thickness-dependent relaxations or interlayer distances that are unacceptably far from experiment, as those reported in Ref.[9]. In fact, as shown in Table 3, the proper orthogonalization of the valence wave-function with respect to the core ones, and the PBE functional --- well-known for outperforming PW for most materials --- improve the agreement with experiment regarding the surface relaxation of the first three interlayer distances. So, while the two potentials certainly yield differences regarding the surface geometry (Table 2 and 3), they are not dramatic as to render either of the two pseudo-potentials useless for applications. The relaxations, which can vary by up to 0.4%, correspond to larger contractions in the PAW-PBE calculations of only ~ 0.01 Å. More importantly, unlike any other previous calculation, both calculations of the first three interlayer relaxations here presented (ultra-soft-PW and PAW-PBE) fit within the experimental error bars. Of course, our PAW-PBE-VASP calculations reproduce better the experimental results, which again suggests that the PAW-PBE is more reliable.

There are also experimental measurements of the relaxation of deeper layers. In Table 3, we compare our converged values of the first, second and third interlayer relaxations (Δd_{12} , Δd_{23} and Δd_{34} , respectively) with those attained from LEED measurements [22] and also with results obtained in previous calculations [3,4,8,9]. As shown, our values slightly and consistently overestimate the experimental ones but none differs from the corresponding measurement as much as some of the values reported in previous works. Moreover, by changing the exchange-correlation functional (PBE instead of PW91) and the ultra-soft Vanderbilt pseudo-potentials by a projected-augmented-wave-method pseudopotential, one finds perfect agreement with experiment as no other work has obtained.

It is worth highlighting that the convergence of Δd_{23} and Δd_{34} is slower than that of Δd_{12} (see Fig.2). This result is unexpected because previous calculations indicate that Δd_{34} approaches to zero, a feature ordinarily taken as indicative that the bulk properties have been recovered. Hence, we conclude that the slower convergence of subsurface interlayer distances speaks for the *thin-*

film limit and thus confirms that properties associated with the *thin-film limit* are harder to converge than the properties exclusive to the surface.

3. Binding and self-diffusion of Mg adatom on Mg(0001)

(a) Adatom binding energy

First of all, we shall test the convergence of the binding energy. **Figure 3** displays the binding energy of a Mg adatom on Mg(0001) at the fcc and hcp sites for slabs of four thicknesses ($N=3,5,7$ and 9). According to our US-PW91-QE calculations, the binding energy of the adatom converges slowly. From $N=5$ to $N=7$, the binding energy drops by as much as 50 meV and from $N=7$ to $N=9$ increases by almost 30 meV. These variations are significant and measurable, but the fact that the surface properties analyzed in Section 2(a) and (b) for 9-layer slabs do not vary dramatically from the converged values, we can safely conclude that the convergent adatom binding energy is ~ 0.6 eV. Our PAW-PBE-VASP calculations confirm that the binding energy is ~ 0.6 eV (0.615 at fcc and 0.601 at hcp) and that is well converged at 7 layers.

The binding of Mg adatoms on Mg(0001) is known to be surprisingly weak. Earlier effective medium calculations [24] yielded that the adatom binding energy is 0.85 eV, only about 57% of bulk Mg cohesive energy. Yet, our calculations indicate that the binding is significantly weaker than previously reported.

(b) Monomer fcc stacking fault preference

First of all, we notice that while convergence of the adatom binding energy down to few meV may require more than 7 layers to converge, the stacking fault energy is well described by 7-layer thick films. This is because the stacking fault energy involves energy differences and these converge more rapidly because the errors in the both binding energy values (at hcp and fcc), which derive from the fact that both quantities are not converged, cancel out each other.

Secondly, we find that the the fcc site (fault site) is energetically more favorable for the adatom than the hcp site **(See Figure 4)**. This result is in contrast with the effective-medium calculations

mentioned above, which reported that the binding energy of Mg adatoms on Mg(0001) is the same at the hcp site as that at the fcc site (They call it, site *unspecificity*). Furthermore, the stacking fault energy favors the fcc site by an unexpectedly large energy: 15 meV. Our PAW-PBE-VASP calculations confirm this value: the adatom stacking fault energy is 13.4 meV and 14.8 meV for 7 and 9 layers, respectively. Note that the stacking fault energy that we find for Mg adatom on Mg(0001) is as large as that found for an Ir adatom on Ir(111) (16 meV [25]). Naturally, the origin of these apparently similar phenomena is completely different and it is worth clarifying it. Ir atoms are held together by particularly strong covalent bonds and thus the favored stacking fault in Ir(111) compensates the low-coordination of the adatom by sitting at the hollow site (hcp) that is directly above another Ir atom instead of sitting at the fcc hollow site (fcc) in which the next Ir neighbor atom directly below is one more layer further away. In diametrical contrast to the above situation, Mg(0001) is a nearly free-electron metal in which the adatom prefers to sit at the infinitely hollow fcc site – site at which no other atom is directly below – rather than at the hcp site that is directly above another Mg atom. In other words, the stacking fault preference in Mg and Ir have opposite effect: Ir adatoms on Ir(111) tend to be overcoordinated while Mg adatom tend to be low coordinated.

4. Mg adatom self-diffusion

Finally, we shall turn to the diffusion barrier of the Mg adatom on Mg(0001). Figure 5(a) shows that, just as in the case of the stacking fault energy, the diffusion barriers from fcc to hcp and from hcp to fcc are also well described by 7-layer thick films. Again, the reason is that energy differences cancel out the errors in the minuend and subtrahend derived from the fact that these quantities are not converged.

The energy barriers (25 and 9 meV) are very small compared to those of any transition metal. The order of magnitude of the barrier is in very good agreement with effective-medium calculations [24], which yielded the two energy barriers to be ~ 20 meV.

Something that calls our attention, however, is that our barrier is quite asymmetric, as shown in Figure 5(b), in contrast to what effective-medium calculations indicate [24]. Thus, our

calculations predict that at sufficiently low temperatures (few Kelvin) the adatom should very rarely be found at the hcp site.

IV. Conclusion

We have performed a first-principles investigation of the structure and surface energy of Mg(0001) free standing films to revise earlier calculations. We have as well examined the adsorption site, binding energy and diffusion barrier of Mg adatoms on Mg(0001) to search for evidence that the predicted size effects may also affect the initial stages of epitaxial growth. Our calculations negate that quantum-size effects produce giant oscillations of the surface properties as a function of film thickness. We find that although overcoming the *thin-film limit* requires more than 23 layers, the surface properties are well converged if the film is ~ 18 layers thick, contrary to the results of Li et al., which have outputted that a film of 20 layers is needed to converge Δd_{12} , and films of more than 30 layers are needed to converge the surface energy. The binding energy of the Mg adatom (~ 0.6 eV) is found to be well converged for 7-layer films and significantly weaker than the value reported by previous calculations. In addition, we find that the fcc-stacking fault is energetically favorable for the Mg adatom by 15 meV. Our calculations also reveal small diffusion barriers for the monomer: 9 meV (hcp to fcc) and 25 meV (fcc to hcp) and are also well converged for 7-layer films, for which size-effects are not expected to influence Mg growth for thicker films.

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TABLE CAPTIONS

Table 1: Calculated (at 0 K) and measured lattice parameters (a and c/a), cohesive energy, and bulk modulus of Mg.

Table 2: Calculated changes (%) in the interlayer distances between the surface layers of Mg(0001) with respect to the bulk value (2.582 Å), $\Delta d_{i,i+1}$, for a 23-layer slab within our US-PW91-QE calculations and our PAW-PBE-VASP calculations (see Section II).

Table 3: Changes (%) in the first (Δd_{12}), second (Δd_{23}), and third (Δd_{34}) interlayer distances of 23 layers of Mg(0001) with respect to the bulk value as rendered by our US-PW91-QE calculations and our PAW-PBE-VASP calculations, previous calculations and experiment.

FIGURE CAPTIONS

Figure 1 (Color online): Calculated energetic and structural properties of Mg(0001) as a function of the number of layers forming the slab, N : (a) Formation energy per atom, $E(N)/N$; the dashed line indicates the cohesive energy of bulk Mg, (b) surface energy and (c) the change (%) in the first interlayer distance with respect to the bulk value, Δd_{12} . In (b) and (c), the dashed line is a guide for the reader indicating the convergent value of surface energy σ and Δd_{12} , respectively. Black squares and grey (red) circles are data from Ref.[9] and the present US-PW91-QE calculations, respectively. Data from Ref.[9] is taken directly from the figure and our data is superimposed at the same scale.

Figure 2 (Color online): Calculated slab thickness dependence of the first, second and third interlayer relaxations, Δd_{12} , Δd_{23} and Δd_{34} , according to our US-PW91-QE calculations. The dashed line for Δd_{12} indicates the convergent value. In the cases of Δd_{23} and Δd_{34} , the dashed line is a guide for the eye of what the convergent value could be.

Figure 3 (Color Online): Slab thickness dependence of the adatom binding energy E_B at the fcc (black squares) and hcp (red circles) sites for slabs of $N=3, 5, 7$ and 9 layers.

Figure 4 (Color Online): Slab thickness dependence of the stacking fault energy, $\Delta E_B = E_B(\text{fcc}) - E_B(\text{hcp})$ for slabs of $N=3, 5, 7$ and 9 layers.

Figure 5 (Color Online): (a) Slab thickness dependence of the adatom diffusion energy barrier, ΔE_D , from fcc to hcp ($\text{fcc} \rightarrow \text{hcp}$, black squares), and from hcp to fcc ($\text{hcp} \rightarrow \text{fcc}$, red circles); (b) Potential-energy profile for adatom diffusion along the diffusion coordinate indicating the binding energy at the fcc, hcp, and transition state (TS) sites, as well as the magnitude of the diffusion energy barriers.

TABLES

Table 1: Calculated (at 0 K) and measured lattice parameters (a and c/a), cohesive energy, and bulk modulus of bulk Mg.

Reference	Lattice parameters		Cohesive Energy (eV)	Bulk modulus (GPa)
	a(Å)	c/a		
This work, PW91	3.213	1.607	1.45	35.48
This work, PBE	3.198	1.625	1.50	
PW [9]	3.201	1.620		
PW [4]	3.18	1.615	1.50	35.5
LDA [3]	3.13	1.616	1.78	40.2
LDA [8]	3.11	1.62	---	---
LDA [18]	3.12	1.616	---	38.4
LDA [19]	3.18	1.623	---	37.7
Experiment [17,21]	3.21	1.624	1.51	35.4
Experiment [20]			---	36.8±3

Table 2: Calculated changes (%) in the interlayer distances between the surface layers of Mg(0001) with respect to the bulk value (2.582 Å), $\Delta d_{i,i+1}$, for a 23-layer slab within our US-PW91-QE calculations and our PAW-PBE-VASP calculations (see Section II).

N	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	Δd_{56}	Δd_{67}	Δd_{78}	Δd_{89}	Δd_{910}	Δd_{1011}	Δd_{1112}	$\Delta d_{12,13}$
QE	2.17	1.12	0.08	-0.03	-0.07	0.13	0.09	0.14	-0.00	0.05	-0.05	-0.05
VASP	1.76	0.74	-0.41	-0.37	-0.15	0.17	0.08	0.10	0.04	0.02	-0.21	-0.21

Table 3: Changes (%) in the first (Δd_{12}), second (Δd_{23}), and third (Δd_{34}) interlayer distances of 23 layers of Mg(0001) with respect to the bulk value as rendered by our US-PW91-QE calculations and our PAW-PBE-VASP calculations, previous calculations and experiment.

	PBE-23L (%)	PW91-23L (%)	LDA-11L (%) [3]	PW-13L (%) [4]	LDA-11L (%) [8]	PW 91-30L (%) [9]	Experiment (%) [22]
Δd_{12}	1.758	2.102	1.13	2.04	1.8	0.7	+1.9±0.3
Δd_{23}	0.744	1.053	0.31	1.13	0.2	-0.9	+0.8±0.4
Δd_{34}	-0.412	0.011	0.21	0.72	-0.3	0.1	-0.4±0.5

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5