Ab initio study of the growth of FCC and HCP nickel thin films on a sapphire substrate

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INTRODUCTION

A thin film is defined as a layer of material ranging from fractions of a nanometer to several micrometers in thickness. Thus, thin films have found their applications in plethora of branches: from oxide semiconductor transistors in organic light emitting diodes (OLED) and liquid crystal displays (LCD) [1] or even paper electronics [2] to thin film silicon, chalcogenide, organometallic dyes or polymer solar cells [3] and composite membranes, used in water and wastewater treatment processes [4, 5]. Moreover, thin film technologies are significant in such materials science branches as multiferroic materials [6] and superlattices [7].

One of the most recent studies conducted by Sharma et al. [8] found that phase separation is present $Ni_{80}Fe_{20}$ films: face-centered cubic (FCC) layers form on the substrate and hexagonal close-packed (HCP) layers form on top of the film. From density functional theory (DFT) calculations it was concluded, that the phase separation in Ni-sapphire system had been driven by the decrease of the film surface and interface energy, because presence of a thin top layer of the HCP phase corresponds to the minimum of the total energy in the system and then the system is in thermodynamic equilibrium. Therefore, equilibrium thickness of the HCP phase forms on top of the FCC film and upper-boundary HCP layer thickness can be calculated by the following inequality:

$$0 < h_H < (\gamma_F - \gamma_H - \gamma_{FH})/(\mathscr{G}_H - \mathscr{G}_F) \qquad (1)$$

where subscripts H and F mean HCP and FCC phases, FH is denoted as FCC/HCP interface, γ is interface or surface energy, while $\mathscr{G}$ refers to the energy per volume of phase.

The aim of this study was to use DFT methods to replicate the results of Ni HCP layer formation on top of FCC layer produced by Sharma et al. [8] and evaluate, if calculations of spin-polarized and non-magnetic Ni produce different outcomes. Furthermore, we aspired to check, whether Co presents the same phenomena and to find a way to quickly determine materials that are likely to develop a surface layer of a different phase.

CONVERGENCE RESULTS

The theoretical investigation was performed using first principle calculations based on fully self-consistent density functional theory (DFT) with the plane wave pseudopotential codes as implemented in the Quantum-Espresso package [9] to compute the structural properties of FCC and HCP Ni and Sapphire. In all the calculations, the exchange correlation term has been determined within the generalised gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof [10]. Self consistency in calculations is achieved until the total energies are converged to 10^{-4} eV/cell and the structures are relaxed until the largest force becomes less than 10^{-2} eV/Å. From all the calculations, we concluded the following convergence parameters: FCC Ni(12x12x12, 160, 910, spin polarised), HCP Ni(10x10x10, 160, 960, spin polarised) and Sapphire(4x4x4, 80, 320, non-magnetic). Relaxation calculations yielded optimum lattice parameters of A=3.5228 Å for FCC Ni and A=2.4893 Å for HCP Ni.

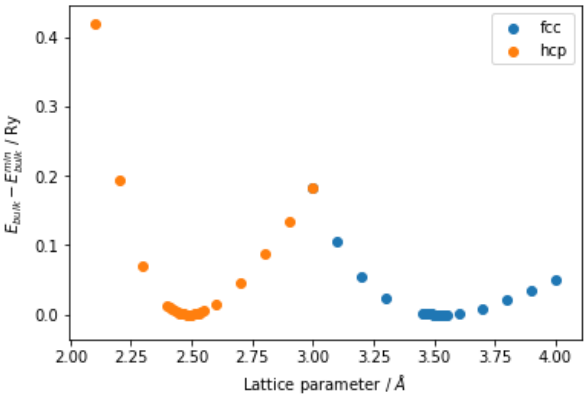

FIG. 1: Plot of Total Energy versus Lattice Parameter for FCC Ni (blue) and HCP Ni (orange).

SURFACE CALCULATION CONVERGENCE RESULTS

The next step consisted in obtaining results of the surface energies for both FCC (111) and HCP (100) Ni surfaces. In order to do so, additional convergence tests needed to be carried out, one with respect to the number of vacuum layers in the supercell and another one with respect to the number of Ni layers in the slabs. Indeed, for the supercell to approximate a surface accurately, sufficient vacuum must be present in order to ensure that neighbouring slabs that arise from periodic

boundary conditions do not interact between each other. The number of Ni layers must also be tested to make sure that central layers are equivalent to bulk layers.

The vacuum thickness convergence was first tested for Ni FCC and HCP slabs made of 3 and 2 atomic layers respectively. These constituted the minimum number of layers necessary to distinguish between FCC and HCP slabs. 1 to 10 layers of vacuum were then added to test convergence. Note that the calculations were always spin polarised, as these require higher convergence thresholds, hence the convergence criteria determined would also be suitable for non spin polarised calculations. Note that for these costly calculations, to increase the computational efficiency, the energy cut-off values and k-meshes were slightly lower than the agreed convergence criteria.

The surface energies γ_x for phase x (HCP of FCC) of Ni for each calculation were computed according to equation 2:

$$\gamma_x = \frac{1}{2A}\left(E_{slab} - n_{slab}E_{bulk}\right), \tag{2}$$

where A is the surface area of the slab, E_{slab} and E_{bulk} are the total energies of the slab and bulk systems respectively and n_{slab} is the number of formal units in the slab. The convergence results are plotted in figure 2. The vacuum layer thicknesses are of 2.034 Å and 2.044 Å for FCC Ni and HCP Ni respectively. The results show that convergence has not been achieved despite taking more than 20 Å of vacuum. Indeed, fluctuations in the surface energy of the order of 0.5 Jm^{-2} are observed for FCC Ni even after 6 layers of vacuum are added. Despite successful consistency check regarding the structure and inputs for the calculations, the issue was not resolved. As a result, no further study could be carried out, as the knowledge on the amount of vacuum required for accurate slab calculations was needed. Reasons for this issue are unclear. Taking a larger size slab may have helped reduce the fluctuations if these are the result of noise.

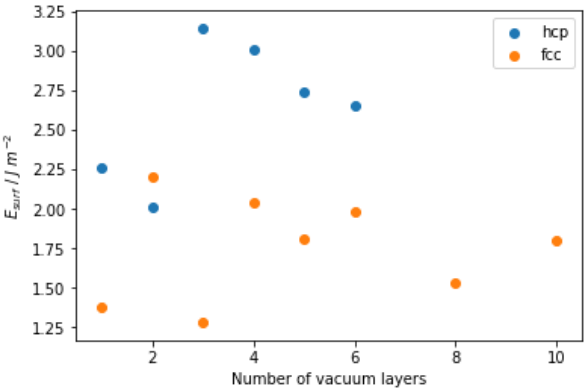

FIG. 2: Plot of surface energy as a function of the number of vacuum layers for FCC slabs (blue) and HCP slabs (orange).

FURTHER WORK

Despite not achieving the desired outcome, an outline of the steps presented in the work plan are given in this section. As indicated in the previous section, the next step would have been to test convergence with respect to the number of Ni layers in the slab. After such tests, suitable vacuum and atomic layer thicknesses would be known for both FCC and HCP slabs. Using these thicknesses, the surface energy for magnetic and non-magnetic slabs of FCC Ni, γ_F, and HCP Ni, γ_H, could then be calculated. This would have to be calculated at a slightly different lattice parameter as discussed below.

The interfacial energy γ_{FH} between FCC Ni and HCP Ni would then have been calculated. Several points need to be considered for these calculations. Firstly, to construct the interface, the FCC and HCP Ni unit cells need to match. For this study, homoexpitaxyl growth would have been assumed, such that the interatomic spacing between atoms in the planes parallel to the interface would be identical in both phases. The choice of this parameter would be determined from the dimensions of the fully relaxed sapphire unit cell. In figure 3, the matching between the sapphire substrate and Ni film is shown. Once this distance is chosen, then convergence tests would need to be carried out with respect to the thickness of both the Ni FCC and Ni HCP films. Once these are obtained, the interfacial energy γ_{FH} could be calculated from equation 3

$$\gamma_{FH} = \frac{1}{2A}\left(E_{slab} - n^F_{slab}E^F_{bulk} - n^H_{slab}E^H_{bulk}\right), \tag{3}$$

where A is the now the surface area of the interface, E_{slab} is the computed energy of the whole system, n^x_{slab} is the number of formal units of phase x in the system and E^x_{bulk} is the bulk energy of phase x [11].

This would constitute the bulk of the energy calculations for Ni. This would have been done for both magnetic and non-magnetic cases. All quantities in equation 1 would be known by this point. Therefore, the maximum thickness h_H of the HCP Ni film could be determined. This would need to be tested against the value of A. Sharma et al. [8], found to be 31 nm computationally and 13 nm experimentally. This limit would then need to be tested by performing calculations of the sapphire/HCP Ni/FCC Ni/vacuum system for HCP Ni thicknesses above and below h_H. It is expected that the energy per atom is lower for the lower thickness than that of the higher one. Ideally a plot of energy against thickness would be obtained. As the thickness of the HCP Ni film is increased, that of the Ni FCC film would need to be decreased accordingly. A problem with checking this

way is of course that the system would be represented as a slab rather than a two semi-infinite solids in contact. One would also need to take many layers of Ni (around 150) to reach a thickness of 30 nm of Ni HCP. It is unlikely these could be carried out.

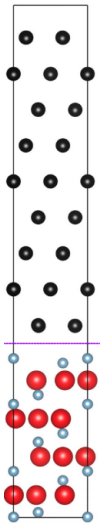

FIG. 3: Supercell of FCC Ni on a sapphire Al_2O_3 substrate, taken from supplementary information of Kumar *et al.* [12]. The black dots are Ni atoms, the red ones O atoms and the blue ones Al atoms.

This would conclude the investigation on Ni. Such steps could be repeated on Co, another 3d ferromagnet. The final task would be to search for other materials that form a small HCP film between the substrate and the bulk FCC (or vice versa). The aim would be to determine which minimum set of calculations would need to be performed to determine whether this phenomenon occurs or not. From inequality 1, the crucial term seems to be γ_{FH}. If it is large and positive, then a HCP film cannot form. Therefore computing this quantity for various elements could be performed to screen the materials with negative or small positive values of γ_{FH}. However this would still involve performing three calculations, bulk FCC, bulk HCP and FCC/HCP interface ones, if convergence criteria are assumed to be the same as for Ni. If one had the insight of the results from from Ni and Co then perhaps it would be easier to determine a smaller set of calculations that could help identify relevant materials.

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