Mechanisms, models and methods of vapor deposition

H.N.G. Wadley a,*, X. Zhou a, R.A. Johnson a, M. Neurock b

aSchool of Engineering and Applied Science, Department of Materials Science, University of Virginia, Thornton Hall, Charlottesville, VA 22903-2442, USA
bSchool of Engineering and Applied Science, Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903-2442 USA

Abstract

The condensation and assembly of atomic fluxes incident upon the surface of a thin film during its growth by vapor deposition is complex. Mediating the growth process by varying the flux, adjusting the film temperature, irradiating the growth surface with energetic (assisting) particles or making selective use of surfactants is essential to achieve the level of atomic scale perfection needed for high performance films. A multiscale modeling method for analyzing the growth of vapor deposited thin films and nanoparticles has begun to emerge and is reviewed. Ab-initio methods such as density functional theory are used to provide key insights about the basic mechanisms of atomic assembly. Recent work has explored the transition paths and kinetics of atomic hopping on defective surfaces and is investigating the role of surfactants to control surface atom mobility. New forms of interatomic potentials based upon the embedded atom method, Tersoff and bond order potentials can now be combined with molecular dynamics to investigate many aspects of vapor phase synthesis processes. For example, the energy distribution of atoms emitted from sputtering targets, the effects of hot atom impacts upon the mechanisms of surface diffusion, and the role of assisting ions in controlling surface roughness can all be investigated by this approach. They also enable the many activation barriers present during atomic assembly to be efficiently evaluated and used as inputs in multipath kinetic Monte Carlo models or continuum models of film growth. This hierarchy of modeling techniques now allows many of the atomic assembly mechanisms to be incorporated in film growth simulations of increasing fidelity. We identify new opportunities, to extend this modeling approach to the growth of increasingly complicated material systems. Using the growth of metal multilayers that exhibit giant magnetoresistance as a case study, we show that the approach can also lead to the identification of novel growth processes that utilize adatom energy control, very low energy ion assistance, or highly mobile, low solubility chemical species (surfactants) to control surface diffusion controlled film growth. Such

* Corresponding author.
E-mail address: haydn@virginia.edu (H.N.G. Wadley).
approaches appear capable of enabling the creation of multilayered materials with exceptionally smooth, unmixed interfaces, with significantly superior magnetoresistance. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Vapor deposition is a highly versatile process that is used to create thin films and coatings for a multiplicity of applications from microelectronics to gas turbine
engines [1]. It is also widely used to grow nanoscale particles [2]. The ability to manipulate the atomic scale structure of thin films and/or nanoparticles during their growth by vapor deposition is enabling the creation of new materials with exceptional functionality such as giant magnetoresistance [3], tunable optical emission/absorption [4], high efficiency photovoltaic conversion [5], and ultralow thermal conductivity [6]. These discoveries are leading to revolutionary devices such as giant magnetoresistive (GMR) sensors and magnetic memories [7], quantum dot lasers and detectors [8], and thermal/chemical protection systems for components operating in hostile environments (e.g. aircraft engine combustion chambers) [9]. Vapor deposition is also at the heart of ongoing efforts to shrink microelectronic circuitry into the nanoscale regime [10], to create functional thin films (e.g. exhibiting high temperature superconductivity, nonlinear optical behavior, and field dependent permittivity/permeability), and to synthesize materials with high thermoelectric figures of merit [11]. Quantum dot arrays containing magnetic atoms may even allow electron spin engineered materials to be devised, potentially opening a route to quantum communications and/or computing [12].

The relatively high cost of this materials processing route [13] is acceptable for these applications because variants of vapor deposition are the only ways to assemble the (often non equilibrium) structures necessary to achieve the needed performance. However, the introduction of many of the products above is paced by the development of processes that enable one to mediate atomic assembly so that appropriate atomic scale structures are created. Success is challenged by the greatly increased chemical complexity and three-dimensional atomic-scale architectures of emerging materials and devices (Fig. 1).

Because of the complexity of vapor deposition, increasing reliance is placed upon modeling and the use of in-situ sensors to achieve the needed atomic scale control. Here, we review the basic elements of a multiscale modeling approach to vapor deposition. Using the growth of GMR multilayers as a case study, we then investigate its use for identification of the critical mechanisms of atomic assembly, for deducing the sensitivity of the mechanisms to the growth conditions, and for exploring the model-based design of novel vapor phase synthesis processes.

2. Multiscale modeling

Vapor deposition is a multiscale process in the sense that growth of the film occurs in a reactor whose dimensions are of O (1 m) for a time of O (10^2 s), while the atomic assembly events involve length scales of O (10^{-10} m) with time scales in the pico to microsecond regime. In fact, atomic assembly is more fundamentally determined by the making and breaking of chemical bonds which is described by the wave functions of bonding electrons with length and time scales of O (10^{-13} m and 10^{-16} s) respectively. Vapor deposition is not unique in this respect — all of materials science confronts a similar issue and many approaches have evolved for treating it [14,15].

The ability to design processes for the growth of an atomic scale structure is critically tied to our ability to connect models with very disparate time and length
Fig. 1. Examples of nanoscale vapor deposited material systems and their critical dimensions.

scales. This ranges from the use of quantum mechanics to describe atomic binding to computational fluid dynamics or discrete simulation Monte Carlo techniques to account for complex flow fields, thermal gradients and reaction environments in the deposition chamber. This modeling hierarchy is summarized in Fig. 2. State of the art modeling and simulation tools such as density functional theory, molecular dynamics, kinetic Monte Carlo and computational fluid dynamics when used alone enable analysis of only a part of a synthesis process. However by using a more fundamental modeling technique to fix the coefficients of the more macroscopic models, or by developing hybrid models that bridge established modeling techniques, the diverse length and time scales of deposition processes can increasingly be spanned. This is leading to more fully predictive growth simulations and the beginning of an acceptance of their use in process design [16]. Both the individual modeling tools and the many techniques for connecting them are under very active development today.

2.1. Ab-initio methods

The advent of powerful computers and improved algorithms has led to the emergence of many ab-initio modeling methods for treating increasingly complex (and realistic) material systems with improving levels of accuracy. Density functional
MULTISCALE MODELING TOOLS FOR VAPOR DEPOSITION

![Diagram showing multiscale modeling tools for vapor deposition]

Fig. 2. The analysis of vapor deposition spans both a wide length and time scale. Overlapping modelling methods are beginning to allow an increasingly rigorous multiscale treatment.

theory (DFT) for ab-initio predictions of atomic scale structure and the analysis of reactions at surfaces has begun to be widely used [17]. Density functional theory is based upon a fundamental observation (provided first by Hohenberg and Kohn) that the total energy of an assembly of atoms is a function of the total electron charge density [18]. Kohn and Sham [19] showed that it is possible to replace the many-electron solution to the Schrödinger equation by an exactly equivalent set of self-consistent one-electron equations — the so called Kohn–Sham equations. This allows the decomposition of the many electron problem into a system of non-interacting electrons moving in an effective potential generated by the nuclei and the other electrons of the system. Iterative methods are then used to compute the self-consistent electric field of an assembly of atoms with fixed atomic coordinates. The procedure yields a total energy for a particular system configuration. By allowing the atom coordinates of the system to vary, it is then possible to find the minimum total energy configuration of systems consisting of several hundred atoms using a modern high performance workstation. The method has reasonable precision. First-principle DFT methods can currently predict binding energies to within a tenth of an electron volt and bond lengths to within 0.02 Å (i.e. to within 1%). It is becoming relatively straightforward to use this method to analyze the kinetics of relevant surface processes, including adsorption, chemical reaction and diffusion. Revolutionary ideas by Car and Parrinello enabled the development of ab-initio molecular dynamics [20,21]. While these simulations are limited to less than a picosecond of real time, they can begin to simulate time-dependent behavior for a wide range of materials because of their first-principles basis. This is a suitable approach for a detailed analysis of the addition of a single atom (or molecule) to a film or particle,
but not for simulating the addition of the thousands or millions of atoms needed to understand how a nanostructure assembles.

As an example of the utility of a first-principles calculation, consider the density functional quantum chemical calculation of the binding energy for a series of different metallic and organic atoms added to a metal surface. The three layer slab shown in Fig. 3(a), was used to model the binding energies and diffusion barriers on ideal Co(0001) terraces. The (4×2)Co(0001) slab depicted in Fig. 3(b) was used to model chemisorption and diffusion along a step edge. The barriers for diffusion were quite sensitive with respect to the specific location of the adatom and its direction of diffusion. We therefore explored adsorption and diffusion along the step edge in the upper plane, away from the step edge on the upper plane, along the step edge on the lower plane, and away from the step edge along the lower plane, of Fig. 3(b). The calculations were performed both unpolarized and polarized to establish the relative magnitude of error associated with neglecting spin polarization. The error, in general, was found to be on the order of 0.2 eV but was quite consistent for most systems.

All calculations were performed using gradient-corrected periodic plane-wave density functional theory. The Vosko–Wilk–Nusair [22] potential was used to calculate the local density exchange and correlation energy. The Perdew–Wang 91

![A) Co(0001)](image)

![B) Co(0001)(4x2)](image)

Fig. 3. Model Co(0001) and (4×2) Co(0001) surface structures that are used in DFT calculations for deducing the binding and diffusion energies on (a) a flat and (b) the step edge of a Co(0001) surface.
potential was used to calculate nonlocal gradient corrections to the exchange correlation energy [23]. Scalar relativistic corrections were incorporated through the use of Vanderbilt ultrasoft pseudopotentials for all atoms [24,25]. A plane wave basis set, used to expand the valence eigenstates, had a minimum kinetic energy of 30 Rydberg. A 4×4×4 Monkhorst k-point representation was used to sample reciprocal space in the first Brillouin zone.

Table 1 shows the calculated results for some metal and metal complex binding energies. The calculated binding energies for atomic Co at the hcp, fcc and bridge sites were −3.97, −3.81 and −3.78 eV, respectively. The preferred adsorption site for a single Co adatom is the hcp hollow site. The energy difference between most of these sites, is however, quite small.

Surface diffusion barriers were calculated as the difference in energy between either the hcp and bridge site or the fcc and bridge site. An adatom optimized at the bridge site is considered herein to be the transition state between the fcc and hcp sites. The barriers for the several representative systems examined are reported in Table 2. The diffusion barrier for Co to hop from the hcp site to the fcc site over a bridging Co–Co bond, is seen to be low with a value of only 0.119 eV. The activation barrier is governed by the metal adatom–surface bond strength. When both the reactant and product states have identical numbers of neighbors (three nearest neighbors out of 12), the barrier is likely to be low. We found this to be true for the diffusion of Co, Au, and Cu adatoms over both Co(0001) and Cu(111) surfaces. Calculated diffusion barriers over the atop adsorption sites were found to be considerably greater than those over the bridge sites. This path requires a change from three bonds between the adatom and the surface to one bond as Co diffuses over the atop site and is therefore a much less likely route.

Table 1
Metal atom and metal complex binding energies (eV) on single crystal Co(0001) and at 4×2 step edges of Co(0001)

<table>
<thead>
<tr>
<th>Adsorbate/surface</th>
<th>Surface</th>
<th>Site</th>
<th>hcp</th>
<th>fcc</th>
<th>Bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co(0001)</td>
<td>Terrace</td>
<td>−3.97</td>
<td>−3.81</td>
<td>−3.78</td>
</tr>
<tr>
<td></td>
<td>4×2 step edge</td>
<td>Top of the step edge</td>
<td>−4.03</td>
<td>−3.81</td>
<td>−3.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom of the step edge</td>
<td>−4.95</td>
<td>−4.40</td>
<td>−4.40</td>
</tr>
<tr>
<td>Co–O</td>
<td>Co(0001)</td>
<td>Terrace</td>
<td>−3.69</td>
<td>−3.49</td>
<td>−3.50</td>
</tr>
<tr>
<td></td>
<td>4×2 step edge</td>
<td>Top of the step edge</td>
<td>−4.10</td>
<td>−3.82</td>
<td>−3.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom of the step edge</td>
<td>−4.53</td>
<td>−4.00</td>
<td>−3.77</td>
</tr>
<tr>
<td>Cu</td>
<td>Co(0001)</td>
<td>Terrace</td>
<td>−3.75</td>
<td>−3.50</td>
<td>−3.29</td>
</tr>
<tr>
<td></td>
<td>4×2 step edge</td>
<td>Top of the step edge</td>
<td>−3.75</td>
<td>−3.50</td>
<td>−3.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom of the step edge</td>
<td>−3.62</td>
<td>−3.43</td>
<td>−3.25</td>
</tr>
<tr>
<td>Au</td>
<td>Co(0001)</td>
<td>Terrace</td>
<td>−3.62</td>
<td>−3.43</td>
<td>−3.25</td>
</tr>
<tr>
<td></td>
<td>4×2 step edge</td>
<td>Top of the step edge</td>
<td>−3.62</td>
<td>−3.43</td>
<td>−3.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom of the step edge</td>
<td>−3.62</td>
<td>−3.43</td>
<td>−3.25</td>
</tr>
</tbody>
</table>

a Unpolarized calculations.
In Table 2, the barriers for diffusion over the ideal single crystal fcc and hcp metal surfaces, as discussed above, were all found to be quite low (compared to $kT$ at typical deposition temperatures), thus indicating that these paths are unlikely to be controlling the surface structure that forms during vapor deposition. Diffusion in the vicinity of defect sites, step edges, kink sites and grain boundaries can be quite different. In particular, adatoms can quite strongly bond to less coordinated edge sites, potentially increasing the energy barrier for diffusion. To examine the effect of coordination on adatom diffusion, we have used the model step edge depicted in Fig. 3(b) to compute activation barriers for diffusion along, and away from step edges. Metal adatoms were placed on the upper level terrace and allowed to move along the ledge as shown in Fig. 4. The diffusion of atomic Co along the step edge of the lower plane (Fig. 5), and away from the step edge on the lower plane (Fig. 6) were also examined. Table 2 shows that these barriers were considerably higher than those for hops on the ideal flat terrace planes of Co(0001). It is a direct consequence of the increased adsorption strength at the step edge.

The binding energy for atomic Co at the hcp hollow site on the upper plane of the step edge is $-4.03$ eV. This is slightly stronger than that for Co at the hcp site on the infinite Co(0001) surface ($-3.97$ eV). The barrier height for Co diffusion along the upper plane at the edge of the step is $0.22$ eV which is only $0.081$ eV higher than that for Co on the infinite Co(0001) plane. The Co adatom binding energy increases to $-4.95$ eV if it is placed at the hcp site at the base of the step edge. The binding
Fig. 4. Diffusion of atomic Co along the top of a step edge on Co(0001) surface. The DFT calculated diffusion barrier was $+0.217 \text{ eV}$.

Fig. 5. Diffusion of atomic Co along the bottom of a step edge on Co(0001) surface. The DFT calculated diffusion barrier was $+0.52 \text{ eV}$. 
energy at the neighboring fcc site at the base of the step edge was calculated to be $-4.40$ eV. The increased adatom binding energies for sites along the base of the step edge are due to the increased number of direct nearest neighbors at the step edge. However, the stronger binding energies also give rise to increased diffusion barriers. The diffusion of atomic Co from the hcp to the fcc step edge over the connecting bridge site was also found to increase from 0.22 eV for diffusion along the top ledge to 0.52 eV for diffusion along the bottom ledge. The barrier height is increased even further to 0.84 eV if Co diffuses away from the ledge on the bottom plane out onto the terrace.

The activation barriers for diffusion are directly related to the strength of the metal surface bond and the change in coordination during an atomic jump. Clearly, the stronger the adatom-surface bond, the more difficult it is to break it in order for diffusion to occur. There is also a dependence between the adatom binding energy and the number of (nearest and next nearest) neighbors. The greater the number of neighbors between the adatom and the surface, the greater is the adsorption energy. For example, the binding energy of Co at the hcp site on a flat terrace (three nearest neighbors) was $-3.97$ eV, whereas a Co atom residing on the bottom plane at the hcp step edge site (five nearest neighbors) has a binding energy of $-4.95$ eV. The fcc step edge site which has an intermediate number of four neighbors has an energy of $-4.40$ eV. The number of next-nearest neighbors has an opposite effect on the calculated binding energy. As the number of next nearest neighbor bonds is increased, the binding energy decreases. This follows the principle of bond-order conservation which suggests that the decrease in the binding energy is the result of an increased
level of bonding between an adsorption site and its nearest-neighbors. This ultimately weakens adatom adsorption. Collectively the number of bonds to a particular site should remain about the same.

2.2. Potentials

Atomic scale structure calculations can be conducted with less computational expense using interatomic potentials in which the electronic degrees of freedom have been “coarse-grained out” by representing the effect of the valence electrons as a bonding dependent on the local environment. Atomistic models using such potentials can be constructed for molecular dynamics studies of vapor deposition and for molecular static calculations to determine the kinetic coefficients involved in the atomic diffusion responsible for film growth. Many potentials have been proposed for this purpose. For metals like those needed in GMR applications, the embedded-atom method (EAM) approach is particularly effective [26–28]. EAM models with an identical analytic form have now been developed for at least fifteen metals: fcc Cu, Ag, Au, Ni, Pd, Pt and Al; bcc Fe, Mo, Ta and W; and hcp Mg, Co, Ti and Zr. These potentials have yielded reasonable fits to the physical properties of all fifteen metals.

The EAM is based on three functions: (1) a two-body pair potential, \( \phi(r) \), which gives the potential energy associated with the bonds between all pairs of atoms, (2) an atomic electron density function, \( f(r) \), for the electron density in the lattice associated with each atom, and (3) an embedding function, \( F(\rho) \), which gives a potential energy arising from embedding a particular atom in the electron density \( \rho \) at its site.

It has been proven that an analytic form for a two body potential between different elements can be constructed based solely on the elemental two-body potentials. This analytical form retains the EAM transformation invariance, and hence allows the models to be normalized. In such models, equilibrium can be attained independently by the two-body energy and the embedding energy [29]. Since the intent of a generalized EAM potential is to use the basic two-body cross potential between different metals to enable the study of a broad range of metallic alloys, including alloys of metals with different elemental structures, a single format was sought for the elemental two-body potentials which is applicable to all the metals under consideration. The generic potentials developed here are normalized in this sense.

Another major difficulty with most atomistic models for metals is that long range potentials are computationally inefficient, and they must be cut off at a certain range for atomistic simulation. However, the cut-off range of the potential and the way the potential is forced to a zero value at this range is a very critical aspect of the potential. It is especially important for alloy models. Little attention is normally given to this problem and this cutoff procedure, but for the generalized model developed here, the fitting of the cut off is an intrinsic part of the potential.

2.2.1. Two-body potential

The underlying form for the generalized two body potential model is a Morse potential, i.e. a combination of a short-range repulsive exponential and a long-range attractive exponential:
\[ \phi(r) = A_e^{-\alpha} \left( \frac{r}{r_e} - 1 \right) - B_e^{-\beta} \left( \frac{r}{r_e} - 1 \right) \]

where \( r \) is the spacing between the two atoms, \( r_e \) is the equilibrium spacing between nearest neighbors and \( A, B, \alpha, \beta \) are four adjustable parameters. With reasonable values of the four parameters for fitting to metallic properties, this potential is much too long-ranged for computer simulation and thus a cutoff procedure must be applied. For this purpose, each term is multiplied by a factor which approaches unity as \( r \) decreases from the cutoff range and approaches 0 as \( r \) increases from the cutoff range. The analytic form chosen to accomplish this is given by:

\[
\phi(r) = \frac{A_e^{-\alpha} \left( \frac{r}{r_e} - 1 \right)}{1 + \left( \frac{r}{r_e - \kappa} \right)^m} - \frac{B_e^{-\beta} \left( \frac{r}{r_e} - 1 \right)}{1 + \left( \frac{r}{r_e - \lambda} \right)^n}.
\]

where \( m, n, \kappa, \lambda \) are four additional parameters. The parameters \( m \) and \( n \) were permitted to vary in the fitting procedure, but it was found that both should be near 20: some metals could not be modeled with a value below 16, and higher values yield a very sharp cutoff. All 15 metals could be fit with both \( m \) and \( n \) equal to 20, so this was taken as a universal value. The repulsive and attractive cutoffs are \( \frac{1}{2} \) when \( r = r_e(1 + \kappa) \) and \( r = r_e(1 + \lambda) \), respectively. Again after much fitting, it was found that \( \lambda = 2\kappa \) provided satisfactory results, so this was also chosen as a universal relation. Finally, many ratios involving \( A, B, \alpha, \) and \( \beta \) were tried. For all cases, \( \alpha/\beta \) was in the range of 1.8 to 2, and the universal choice of 1.875 was made. Thus, although four parameters were introduced with the cutoff factors, there was little flexibility available for fitting to metallic properties and four universal relations were found, leaving four adjustable parameters.

The cubic two-body potentials were fitted to the lattice constant, to the Voigt average shear modulus, to the elastic anisotropy ratio, and (approximately) to the vacancy formation energy. There is not an explicit anisotropy ratio for hcp metals so \( \lambda = 1 \) was used as the fourth condition for the four hcp metals. Both fcc metals and bcc metals have cubic elastic constants and therefore the same input properties. The model yields the stable structure for all the cubic metals studied, i.e. the stable structure is an output, not an input. The cutoff range is smallest for bcc metals, intermediate for fcc metals, and longest for hcp metals.

2.2.2. Electron density function

The electron density function is taken with the same form as the attractive term in the two-body potential with the same value of \( \beta, \lambda, \) and \( n \), i.e.

\[
f(r) = f_e e^{-\beta} \frac{\left( \frac{r}{r_e} - 1 \right)}{1 + \left( \frac{r}{r_e - \lambda} \right)^n}
\]
The value of $f_c$ has no effect on the calculation of any elemental property, but does affect alloy properties when the basic alloy cross potential is used. There is a dearth of alloy data for fitting purposes so minor adjustments may be made in the future, but taking $f_c$ as proportional to the cohesive energy and inversely proportional to the characteristic length $\Omega^{1/3}$ ($\Omega =$ atomic volume) leads to realistic results. With this choice, the electron density functions for the various metals require no additional fitting parameters.

2.2.3. The embedding function

The data for fitting an embedding function pertain to properties at equilibrium, i.e. the embedding function evaluated at equilibrium electron density $\rho_e$ A standard form for the embedding function is

$$F(\rho) = F_c \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right)^{\eta} \right] \left( \frac{\rho}{\rho_e} \right)^{\eta}$$

There are two adjustable parameters, $F_e$ and $\eta$, which are determined from the cohesive energy ($E_c$) and the bulk modulus. This form provides equilibrium (zero slope evaluated at $\rho_e$), has zero value at $\rho = 0$ and is physically reasonable at large $\rho$ (short interatomic distances). However, it approaches zero value at $\rho = 0$ with infinite slope and yields poor values for the pressure derivative of the bulk modulus. The pressure derivative of bulk modulus is a dimensionless number with values in a narrow range near 4–5 for metals while the above form (coupled with the two-body potential) gives either much larger or much smaller results with seemingly no systematic variation.

Thus, a simple cubic equation was used for the embedding function near equilibrium electron density. The four parameters in the cubic equations were determined from equilibrium, and are fitted to the cohesive energy, the bulk modulus and the pressure derivative of the bulk modulus. This pressure derivative is not known for all the metals being considered, so the value calculated from a universal equation of state in the literature [30] was used. To retain the properties of the above equation at large $\rho$, it was fitted to the cubic equation with matching value and slope at $\rho = 1.15 \rho_e$ and used at larger $\rho$. To give zero value at $\rho = 0$, another cubic equation which does have zero value at $\rho = 0$ was splined (matched with value, slope and concavity) to the first cubic equation at $\rho = 0.85 \rho_e$. The second cubic equation was used for $\rho < 0.85 \rho_e$. This scheme seems somewhat complex, but yields smooth embedding functions that match appropriate physical criteria in all cases:

$$F(\rho) = \sum_{i=0}^{3} F_{i} \left( \frac{\rho}{\rho_n} - 1 \right)^{i} \quad \rho < \rho_n \quad \rho_n = 0.85 \rho_e$$

$$F(\rho) = \sum_{i=0}^{3} F_{i} \left( \frac{\rho}{\rho_e} - 1 \right)^{i} \quad \rho_n \leq \rho < \rho_o \quad \rho_o = 1.15 \rho_e$$
\[ F(\rho) = F_0 \left[ 1 - \ln\left( \frac{\rho}{\rho_c^\eta} \right) \left( \frac{\rho}{\rho_c^\eta} \right)^{\eta} \right] \eta_0 \lesssim \rho \]

The universal parameter values and relationships used for fitting are listed in Table 3. As examples, the specific parameters for Cu, Au, Ta, and Co are listed in Table 4.

2.2.4. Functional shapes

As an example of the shape of the functions, the two-body potentials for Cu, Au, Ta, and Co and the two-body cross potentials for Cu–Au, Cu–Ta and Cu–Co are shown in Fig. 7. Note that the energy well for the cross potential can be deeper than that for either component, which gives rise to the binding of intermetallic compounds.

2.2.5. \(L_12\) intermetallic compounds

The change in energy per atom (in eV) in going from a block of pure metal A with \(3N\) atoms and a block of pure metal B with \(N\) atoms to a block of intermetallic compound \(A_3B\) with \(4N\) atoms is given in Table 5. The upper value is from the

| Table 3 |
| The universal relations used in the fitting EAM potentials |
| \(\lambda = 1.875\beta\) | \(\lambda = 2\kappa\) | \(m = 20\) | \(n = 20\) |
| \(f_c = E_c/\Omega^{1/3}\) | \(\rho_n = 0.85\rho_c\) | \(\rho_o = 1.15\rho_c\) |

<p>| Table 4 |
| EAM parameters for various metals |</p>
<table>
<thead>
<tr>
<th>Cu</th>
<th>Au</th>
<th>Ta</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_c (\text{Å}))</td>
<td>2.556162</td>
<td>2.885034</td>
<td>2.860082</td>
</tr>
<tr>
<td>(f_c (\text{eV/Å}))</td>
<td>1.554485</td>
<td>1.529021</td>
<td>3.086341</td>
</tr>
<tr>
<td>(\rho_c (\text{eV/Å}))</td>
<td>22.150141</td>
<td>21.396373</td>
<td>33.787168</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>7.669911</td>
<td>8.086176</td>
<td>8.489528</td>
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<td>(\beta)</td>
<td>4.090619</td>
<td>4.312627</td>
<td>4.527748</td>
</tr>
<tr>
<td>(A (\text{eV}))</td>
<td>0.327584</td>
<td>0.230728</td>
<td>0.611679</td>
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<tr>
<td>(B (\text{eV}))</td>
<td>0.468735</td>
<td>0.336695</td>
<td>1.032101</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>0.431307</td>
<td>0.420755</td>
<td>0.176977</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>0.862614</td>
<td>0.841511</td>
<td>0.353954</td>
</tr>
<tr>
<td>(F_{\text{A0}} (\text{eV}))</td>
<td>−2.176490</td>
<td>−2.930281</td>
<td>−5.103841</td>
</tr>
<tr>
<td>(F_{\text{A1}} (\text{eV}))</td>
<td>−0.140035</td>
<td>−0.554034</td>
<td>−0.405524</td>
</tr>
<tr>
<td>(F_{\text{A2}} (\text{eV}))</td>
<td>0.285621</td>
<td>1.489437</td>
<td>1.112997</td>
</tr>
<tr>
<td>(F_{\text{B0}} (\text{eV}))</td>
<td>−1.750834</td>
<td>−0.886809</td>
<td>−3.585325</td>
</tr>
<tr>
<td>(F_{\text{B1}} (\text{eV}))</td>
<td>−2.19</td>
<td>−2.98</td>
<td>−5.14</td>
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<tr>
<td>(F_{\text{B2}} (\text{eV}))</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(F_{\text{B3}} (\text{eV}))</td>
<td>0.702991</td>
<td>2.283863</td>
<td>1.640098</td>
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<tr>
<td>(\eta)</td>
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<td>0.494127</td>
<td>0.221375</td>
</tr>
<tr>
<td>(F_{\text{C0}} (\text{eV}))</td>
<td>0.921150</td>
<td>1.286960</td>
<td>0.848843</td>
</tr>
<tr>
<td>(F_{\text{C1}} (\text{eV}))</td>
<td>−2.191675</td>
<td>−2.981365</td>
<td>−5.141526</td>
</tr>
</tbody>
</table>
Fig. 7. The pair potentials of copper, gold, cobalt and tantalum and several of their cross potentials used in an alloy form of the EAM potential.

Table 5
The change in energy (eV/atom) to create \( A_3B \) compounds

<table>
<thead>
<tr>
<th>Majority atom</th>
<th>Minority atom</th>
<th>Copper</th>
<th>Silver</th>
<th>Gold</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Copper</td>
<td>0.096</td>
<td>−0.059</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>Copper</td>
<td>0.086</td>
<td>−0.065</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>Silver</td>
<td>0.076</td>
<td>0.011</td>
<td>0.206</td>
<td></td>
</tr>
<tr>
<td>−0.043</td>
<td>−0.044</td>
<td>0.233</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Gold</td>
<td>−0.034</td>
<td>−0.046</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>0.039</td>
<td>Nickel</td>
<td>0.019</td>
<td>0.314</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>0.251</td>
<td></td>
<td>0.039</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The present model and the lower is from an ab-initio calculation [31,32]. Relaxation of the atomic volume from the value given by Vegard’s Rule has been calculated and is minor.

Many other computationally efficient potentials are also being developed for other material systems [33]. For example, Pettifor has developed a novel theory that allows many body, angularly-dependent interatomic potentials to be derived directly from a tight binding description of the electronic structure [34]. The theory is based on the familiar idea of coarse graining the electronic structure through its moments and then relating the \( p \)th moment to the sum over all bonding paths of length \( p \) that start and end on a given atom [35]. The uniqueness of the theory is that it provides the only rapidly convergent method for evaluating the bond order of a given bond in terms of the first few moments. These bond order potentials (BOPs) have been shown to give a quantitative description of single, double, triple and conjugate bond behavior amongst the hydrocarbons [36], and the correct deformation behavior of bcc and hcp transition metals and high temperature intermetallics [37,38].
2.3. **Molecular dynamics**

Interatomic potentials can be used in molecular dynamics to analyze various mechanisms of vapor deposition [39,40]. In this approach, Newton’s equations of motion are solved for all the atoms in an ensemble using an interatomic potential to calculate the forces. The method computes the position and velocity of every atom in the system at time intervals short compared to the highest lattice vibration period. Lagrangian schemes allow computation of internal stress, and thermostat algorithms can be used to control the temperature. Interatomic potentials of the type described above for metals have been used in 3-D molecular dynamics (MD) codes to explore the mechanisms and characteristics of sputtering by inert gas ions, transient atomic reassembly during energetic adatom or neutral species impact with a film [41,42], and to relate atomic scale structures to deposition conditions [43]. However, it is important to recognize that the use of short MD time steps (about a femtosecond) to model high frequency lattice vibrations, coupled with the large number of atoms that must be deposited (to obtain a reasonable volume that reveals a microstructure), results in a need to use high deposition rates. The unrealistically high deposition rates may therefore predict a more kinetically trapped structure than is likely to occur in practice. Voter [44], and most recently Orszag and Goldhirsh at Cambridge Hydrodynamics [45] are developing acceleration schemes for molecular dynamics which may eventually enable these limitations to be at least partially overcome.

2.4. **Kinetic Monte Carlo methods**

Kinetic Monte Carlo (k-MC) simulation offers an alternative to molecular dynamics for predicting film scale structure, provided that the mechanisms of growth have been established beforehand. The method is in principle simple, and many variants of the k-MC method have been developed [46]. The method proceeds by first identifying the important steps (mechanisms) of atomic absorption and diffusive assembly on the growth surface. Fig. 8 shows some examples. The rate at which each jump happens is then characterized by a jump activation barrier and a jump attempt rate. An Arrhenius kinetic expression is used to compute the resulting jump probability. The activation barriers can be computed using an ab-initio method such as density function theory or a molecular statics (MS) analysis of the system’s total energy as a function of jumping atom position along a transition path [47]. Fig. 9 shows examples of the (MS) computed activation barriers for a 2-D model of nickel. Twenty-two different jump paths have been identified.

During simulation of vapor deposition, a new atom is added to a substrate at \( t = 0 \). The probabilities, \( P_i \), of all jumps that can be taken by the system are computed using \( P = v_0 \exp \left( -\frac{E_i}{kT} \right) \) where \( v_0 \) is the jump attempt frequency, \( E_i \) the activation barrier for a jump \( i \), \( k \) is Boltzmann’s constant and \( T \) the absolute temperature. The inverse of \( P_i \) is the residence time (between jumps of that type). Probabilistic methods are used to select a surface jump event. This is allowed to occur (and the atom configuration updated), and an average time required for the
system to make the event is subtracted from the time interval between atom arrivals. This continues until sufficient time no longer exists for further reorganization of the structure. A new atom is then added and the process repeats. The Arrhenius expression for atomic jumping introduces the role of substrate temperature, the time interval between atom arrivals fixes a deposition rate, and the direction of the ballistically added atoms defines an incident flux angle [46]. Techniques have also been proposed to include the effects of adatom kinetic energy [48].

Srolovitz and others have recently shown that when the rates of competing reaction pathways are known, k-MC codes can also be used to simulate chemical reaction paths on surfaces. They have used it to simulate the chemical vapor deposition (CVD) growth of diamond which involves many parallel surface reactions each with a unique reaction rate and activation barrier [49]. This has enabled the prediction of the diamond film’s growth rate, grain boundary evolution, and surface morphology transition as gas phase reactant concentrations and temperatures are varied. Remarkable agreement with independent experiments has been achieved.

2.5. Hybrid methods

Atomic simulations are too computationally intensive to permit their use for analyzing structural evolution at the micrometer length scale over the many minutes of processing typical of practical deposition processes. Models based upon continuum...
### Table

<table>
<thead>
<tr>
<th>Jump</th>
<th>Configurational transition</th>
<th>Bonds (from - to)</th>
<th>Energy barrier (eV)</th>
<th>Residence time (sec) (at 350K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2 - 2</td>
<td>0.44</td>
<td>4.28 X 10^{-7}</td>
</tr>
<tr>
<td>2 (a)</td>
<td></td>
<td>2 - 3</td>
<td>0.38</td>
<td>5.86 X 10^{-8}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>3 - 2</td>
<td>0.91</td>
<td>2.47</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3 - 3</td>
<td>0.85</td>
<td>0.34</td>
</tr>
<tr>
<td>4 (a)</td>
<td></td>
<td>2 - 4</td>
<td>0.31</td>
<td>5.77 X 10^{-9}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>4 - 2</td>
<td>1.34</td>
<td>3.79 X 10^{9}</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>4 - 4</td>
<td>0.96</td>
<td>12.94</td>
</tr>
<tr>
<td>6 (a)</td>
<td></td>
<td>3 - 4</td>
<td>0.71</td>
<td>3.28 X 10^{-3}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>4 - 3</td>
<td>1.21</td>
<td>5.11 X 10^{4}</td>
</tr>
<tr>
<td>7 (a)</td>
<td></td>
<td>4 - 5</td>
<td>0.48</td>
<td>1.61 X 10^{-6}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>5 - 4</td>
<td>0.93</td>
<td>4.79</td>
</tr>
<tr>
<td>8 (a)</td>
<td></td>
<td>3 - 5</td>
<td>0.20</td>
<td>1.51 X 10^{-10}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>5 - 3</td>
<td>1.02</td>
<td>94.48</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>5 - 5</td>
<td>0.70</td>
<td>2.35 X 10^{-3}</td>
</tr>
<tr>
<td>10 (a)</td>
<td></td>
<td>2 - 5</td>
<td>Spontaneous</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td>5 - 2</td>
<td>Unstable, &gt;1.30</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>3 - 3 bulk</td>
<td>0.80</td>
<td>6.46 X 10^{-2}</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>5 - 5 bulk</td>
<td>0.83</td>
<td>0.17</td>
</tr>
<tr>
<td>13 (a)</td>
<td></td>
<td>2-3 via 2-4 &amp; 4-3</td>
<td>0.57, Reverse 1.06</td>
<td>3.17 X 10^{-5}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td>3.56 X 10^{2}</td>
</tr>
<tr>
<td>14 (a)</td>
<td></td>
<td>2-3 via 2-1-3</td>
<td>0.66, Reverse 1.15</td>
<td>6.25 X 10^{-4}</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td>7.01 X 10^{3}</td>
</tr>
</tbody>
</table>

Fig. 9. EAM calculated activation barriers for atomic jumps on a 2D nickel surface.

Concepts are used for this. For example, grain growth or phase transformation kinetics can be analyzed by phase field techniques. Diffusion with or without simultaneous reactions can be analyzed using partial differential equation techniques. However, these approaches do not introduce an explicit dependence upon the rate of deposition or other parameters of the fluxes. Recent work has begun to explore methods for linking the many continuum models used to analyze microstructural evolution to atomic scale simulations. For example, by combining molecular dynamics simulations of vapor deposition at high rates with vacancy diffusion models [50] or with Cahn–Hilliard analyses of boundary migration [51], predictions of structure at realistic deposition rates have been deducted.

As an example of such a hybrid modeling approach, consider the molecular dynamics simulation of a copper/cobalt/copper multilayer at a deposition rate of
1nm/ns where the atoms have a kinetic energy of 0.1 eV (Fig. 10). By coloring three adjacent layers in the [111] growth direction and superimposing the layers, [Fig. 10(a) and (b), it is possible to observe the presence of stacking faults (regions of hcp stacking in copper and fcc stacking in normally hcp cobalt). At the high deposition rate of the simulation, the boundaries between faulted and unfaulted domains on the (111) plane have not had an opportunity to migrate as far as they would in a more realistic, lower deposition rate experiment. Phase field techniques can be used to analyze this migration, but they require knowledge of the energy and mobility of the twin interface and the twin domain boundary. These can be obtained from molecular dynamics and molecular statics simulations. Fig. 11 shows an example result from the migration of stacking faults on the (111) surface of the copper layer. Good agreement has been obtained between the simulated twin structure of (111) vapor deposited copper and those observed experimentally [52]. Interestingly, the simulations predicted that the final twin structure is weakly sensitive to the rate or temperature of deposition. Extension of the approach to treat the dependence of twin structure upon other attributes of the deposition processes (e.g. angle of incidence, impact energy, ion assistance conditions) has not been attempted, nor has the model been applied to other microstructural changes such as grain growth or the precipitation of second phases. Many other classical models of microstructural evolution are amenable to this hybrid approach. One example is the use of level sets methods for modeling surface morphology during the growth of thin films [53].
Fig. 11. Temporal evolution of stacking faults during vapor deposition. The light region corresponds to a faulted lattice. The temperature was 520 K.

2.6. Reactor scale models

Numerous approaches have been developed for analyzing thermal and atomic transport in deposition systems. The discrete simulation Monte Carlo (DMSC) method has proven to be particularly appropriate under the rarefied conditions encountered in most physical vapor deposition processes [54]. Several groups have explored this approach for CVD and have developed mature reactor-scale codes that can be used to both understand the deposition process and to inspire the development of deposition routes that improve process outcomes [55]. The DSMC method has recently been used to model the transport of binary mixtures of inert gases and atomically dispersed metals during jet and directed vapor deposition processes [56]. The DSMC methodology is also being used to model aspects of sputtering and plasma enhanced CVD. In these cases, atoms and energetic neutrals propagate through a rarefied plasma prior to deposition on a substrate. DSMC methods can account for the effects of scattering upon both fluxes [57,58]. Models developed by Kushner et al. [59,60] also address ionization of sputtering gases, compute incident ion energy and angle over complex target surfaces, and enable prediction of the atom emission rate over a target surface (i.e. the sputter erosion profile), all as a function of process geometry and operating parameters.
Fig. 12. A comparison of a multiscale simulation of the RF diode deposition of 2000 Å thick copper films with atomic force micrographs of samples grown under identical conditions.

Several groups are attempting to couple reactor scale models with atomistic simulations to predict values and variances in film thickness, structure, and defects across large substrates or to explore the ways in which changes to the operating conditions of a process can be used to affect film parameters. Fig. 12 shows an example of the predicted change in surface roughness as the operating conditions of an RF diode deposition process are changed [61]. It is compared with atomic force microscopy images of 2000 Å thick copper film grown under the modelled conditions. The simulation coupled a continuum plasma model with a reactor geometry and MD sputter analysis to compute the atomic copper flux emitted from a target. DSMC then propagated the atoms through the working gas and hyperthermal k-MC code was used to assemble an atomic structure. The trend in surface roughness of the simulation and the measurements are similar.
Fig. 13. An illustrative GMR device showing the composition and thickness of the many metal layers. In this example, the NiFe/Co layers are magnetized. The moment of the bottom NiFe/Co magnetic is pinned (by the NiO layer), but others are able to rotate in response to a weak applied magnetic field.

3. Magnetic multilayers

In 1988, magnetic multilayers synthesized by physical vapor deposition were found to exhibit very large (several percent) changes in their electrical resistance when a moderate magnetic field was applied [62]. This giant magnetoresistive (GMR) effect has led to the emergence of devices for sensing magnetic fields. A schematic illustration of such a device is shown in Fig. 13. Fig. 14 shows a measured resistance versus magnetic field hysteresis curve for a small (1.5 × 15 μm) NiFeCo/CoFe/Cu/CoFe/NiFeCo spin valve synthesized by Motorola. This sample exhibits resistance change of 5.3% [63]. The GMR effect is typically characterized by the GMR ratio defined by the maximum resistance change divided by the resistance at magnetic saturation. The resistance change arises from a drop in spin dependent electron scattering when an applied field aligns the magnetic moments of the ferromagnetic (CoFe) layers on either side of a 20–30 Å thick Cu layer.

Fig. 15 schematically shows the band structure of a GMR device. In a normal (non magnetic) metal, such as copper, the band structure of the two electron spins (spin up and spin down) of the conduction electrons is identical. However, in a ferromagnetic metal such as cobalt, the energy of the two bands is displaced. When the magnetic moments of a Co/Cu/Co sandwich are aligned, electrons of one spin are able to propagate across the interfaces without scattering and the resistance is low. When the magnetic moments are not aligned, the electrons are spin scattered because the only available energy band is for electrons of opposite spin. As a result, the resistance is higher.
The magnitude of the resistance change strongly affects device performance. It depends upon many factors. While a basic theory is emerging, a detailed model still needs to be developed in order to predict the effects of changes to the material system, the layer thicknesses, microstructure parameters such as texture and grain size, defects such as voids, vacancies, and dislocations as well as residual stress upon the spin dependent electron transport behavior.

Intensive experimental research has led to the discovery of complex multilayered systems exhibiting room temperature resistance changes of 30% or more when relatively weak (< 100 Oe) saturation fields are applied. Some Co/Cu/Co-base systems have recently exhibited GMR ratios of 80%, though the fields needed are also higher (~10^4 Oe). Magnetic field sensors based upon GMR spin valves are now used in the read heads of hard disks, and their use for magnetic random access memory (MRAM) is also being investigated. Fig. 16 shows a proposed architecture for magnetic random access memory [64]. The magnetic moment directions can be set with electric current pulses and the stored data (i.e. the alignment of the ferromagnetic layer) can be read by the changed electrical resistance. A race has now begun to bring these new devices to market. Already the first 256 KB memories have been
manufactured at Honeywell. Scaling calculations indicate that this new magnetic form of nonvolatile memory will be able to reach 4 GB capacity within 10 years, at which point it may successfully compete with DRAM in terms of storage density, access speed and cost. These applications appear to be the first in a new era of “spintronic” device technology that exploits the “spin” property of electrons.

The device applications described above require materials with a high GMR ratio, a low sheet resistivity, a low saturation magnetic field \( H_s \), a linear field dependence, a weak temperature dependence in the ambient temperature range and thermal stability during subsequent process steps [65]. While many multilayered systems have been discovered to exhibit the GMR effect, efforts to tailor material systems to maximize device performance are still in their infancy. Of the many systems under study, the Co/Cu/Co system is attracting the greatest interest because of its high GMR ratio and low saturation field [66]. Though first discovered in the Fe/Cr system, subsequent GMR research has explored Fe/Cu, Co/Cr, Co/Cu, NiFe/Cu/Co, NiFe/Cu/NiFe, NiFe/Ag/NiFe, Cu/NiFeCo and Au/NiFe. Over time, layer architectures have become increasingly complex [67].
Fig. 16. The architecture of magnetic random access memory and the means for reading the data. The storage elements consist of GMR metal multilayers or magnetic tunnel junctions. The magnetic moment of some of the magnetic layers are pinned while others in each storage element are set by applying a magnetic field to them. The magnetic state of each cell can be read by passing a weak current along a word line, through one element, and out along a bit line (courtesy of S. Parkin).

The GMR ratio, saturation field, etc., have been found to be a very sensitive function of the chosen material system, the layer thickness, the processing method, and the conditions used for deposition. For instance, the GMR ratio has an oscillatory dependence upon the Cu layer thickness [68,69]. The maximum GMR ratio is seen at a copper spacer thickness of 10 Å, but layers of this thickness require a high saturation field to achieve the large GMR ratio. A second GMR peak at a thickness of around 25 Å is much better suited to device applications. The dependence of the GMR ratio upon layer thickness is very strong. Even a monolayer change in the thickness of the Cu spacer layer can result in a large decrease in GMR ratio, which adversely affects many potential uses.

Other effects on the GMR ratio have also been noted. For example, changes in the Ar pressure, the bias voltage or the base pressure of sputter deposited films all result in large GMR changes. Significant differences between the GMR responses of MBE, ion-beam-deposited, and sputtered films are also common. Lastly, even though most samples have been deposited on wafers of 50 mm diameter or less, considerable spatial non-uniformity in their spin dependent properties is often seen. The origins of these effects are thought to lie in local changes in the film’s thickness, crystallinity/texture, interface roughness, extent of interdiffusion (chemical roughness), intrinsic
stress, impurity incorporation, as well as atomic scale line (such as dislocation) and planar (such as stacking) defects. Recent analyses of electron transport indicate that maintaining a flat unmixed interface is particularly important.

4. Inert gas ion sputtering

Variants of sputtering are widely used for growing GMR multilayers. Sputtering involves the emission of atoms from a solid surface following energetic particle (atom or ion) bombardment. In the sputter deposition processes used to grow GMR films, high energy (500–2000 eV) argon or xenon gas ions bombard a metal target to induce sputtering. The resulting atomic metal flux propagates to a substrate where it is deposited. During ion beam deposition, the high-energy inert gas ions that bombard the target can be reflected as neutrals. These neutrals can also reach the substrate and modify the atomic assembly of the film. In diode and/or magnetron sputtering, significant inert gas ion fluxes with energies in the 50–200 eV range also irradiate the growth surface. The structure of vapor deposited films is sensitive to the fluxes of the metal and inert gas atoms/neutrals, their incident energies, their incident angles, and their spatial distributions. It is therefore important to determine these sputtered flux attributes in order to later explore how to optimize a sputter deposition process. Specifically, knowledge about the sputtering yield of the metal target, the reflection probability for the bombarding ions, the energy and angular distributions of both the sputtered atoms and the reflected neutrals are all highly desirable.

Sputtering and reflection are affected by many factors at the atomic scale. An incoming bombarding particle colliding with a target surface can either reflect or become trapped in the target, as it transfers a fraction of its energy to the target atoms with which it collides. If the energy transferred to a target atom is more than its binding energy at the lattice site, a primary recoil atom is created. The primary recoil atom can collide with other target atoms, distributing the energy via a collision cascade. A surface atom becomes sputtered if the energy it acquires has a vibrational component pointing out of the surface that is larger than the surface binding energy. The binding energy depends upon the local atomic perfection of a surface since isolated atoms on terraces or those at ledges or kinks are less strongly bound.

The collision cascade evolution is also influenced by the crystal lattice structure through which channeling, blocking, and focusing can occur. Consequently, sputtering is a sensitive function of target surface structure and the crystal orientation relative to the incident direction of the bombarding particle [70–72]. Sputtering and reflection are also sensitive to the bombarding energy, the bombarding angle, the bombarding particle species, the atomic weight of the target atoms, and the target surface structures [72–75], because these parameters define the energy and momentum transfer during the bombardment. The problem becomes even more complicated because the target surface morphology evolves during sputtering (through preferential atom ejection and surface diffusion), and this can dramatically change the local incident angle of a bombarding event, and therefore the character of the sputtered flux.
Because a multidimensional space must be explored, it is difficult to characterize sputtering using only experiments. Extensive theoretical studies of the problem have therefore been conducted [76,77]. These studies have identified three collision cascade regimes: the single-knock-on regime where a low energy and light bombarding particle induce a very diluted collision cascade involving only a few atoms; the linear-cascade regime where a medium energy (or high mass) bombarding particle causes a larger and denser cascade; and the collision-spike regime where a high energy particle impact results in a very dense cascade in which each target atom may be knocked on while it is already in motion. To fully describe the atomic nature of these sputtering processes, atomistic simulation approaches must be applied.

One approach has used a binary-collision approximation (BCA) in which every moving atom was assumed to collide with only one target atom at a time. Monte Carlo (MC) methods have then been used to simulate the linear collision cascade [78–80]. An example is the TRIM simulation method [79,80]. However, these methods suffer serious drawbacks. Firstly, they require a number of simulation parameters (such as surface or bulk binding energies) which are sometimes unclear and have to be fitted to experimental data. Secondly, real sputtering often occurs outside the linear-cascade regime: zones of high energy density (spikes), where moving atoms interact with other moving atoms, exist even for a relatively low energy sputtering event; larger cluster sputtering is also possible; and chemical effects such as those encountered in ion beam etching or compound sputtering also often occur. Thirdly, traditional MC methods cannot give accurate results for the energies of the sputtered atoms and reflected neutrals.

The molecular dynamics (MD) method can be used to address all of the sputtering phenomena that occur within a short time following the ion bombardment. MD simulations have become widely used due to advances in computer power and the emergence of good interatomic potentials. Because the trajectories of all target atoms and the impinging particles are traced by integrating Newton’s equations of motion, the multiple collision (spike) regime is not any more difficult to simulate than the linear regime. Cluster emission, the angular and energy distributions of sputtered atoms and reflected neutrals (or any other events), are all natural solutions of a MD simulation. If the potentials incorporate chemical bonding effects, even chemical effects in sputtering can be simulated [81–84].

As an example, we have used a molecular dynamics simulation approach to explore the Ar$^+$ ion induced sputtering of a [111] fiber textured Ni target. An embedded atom method (EAM) potential [85] was used to define the interaction between the Ni atoms, and a universal potential [86] was used to calculate the interaction between the Ar$^+$ ions and the Ni atoms. The EAM potential accounts for the local environment effects on the atomic binding energy, and hence can produce better results than traditional pair potentials [87,88]. The universal potential can realistically describe the sputtering process because it has been fitted to the extensive experimental data for energetic particle bombardment of solid surfaces.

The computational Ni crystals contain 60 (224) planes in the $x$ direction, 30 (111) planes in the $y$ direction, and 36 (220) planes in the $z$ direction. A small part of the crystal is shown in Fig. 17. The Ar$^+$ ion was assumed to behave like an Ar atom
Fig. 17. The geometry used for a molecular dynamics simulation of the sputtering of a nickel crystal by argon.

during impact. An impact was simulated by injecting an Ar atom with a designated incident energy, $E_{Ar}$, and incident direction from a random position far above the crystal surface. The full three-dimensional impact direction was defined by the incident angle, $\theta$, and an azimuth angle, $\phi$. By randomly varying $\phi$, sputtering from a (111) fiber textured polycrystalline Ni surface was simulated. During the simulation, periodic boundary conditions were used in the $x$ and $z$ directions to extend the horizontal crystal dimensions. The bottom ($y$) monolayer atoms were fixed at their equilibrium positions to prevent crystal shift during impact, and a temperature control scheme [89] was used to maintain the two monolayers immediately above the fixed region at a constant temperature of 300 K. Information such as the sputtering yield of target atoms, the reflection probability of neutrals, the energy and angular distribution of sputtered atoms and reflected neutrals, were accumulated by analyzing from 50 to 500 impact simulations at each Ar ion incident energy and incident angle.

Simulations were conducted for a variety of incident energies and incident angles. Fig. 18 shows an example of the energy distribution of the sputtered Ni atoms at an incident Ar energy of 0.9 keV and a normal incident angle ($\theta = 0^\circ$). Experimental energy distributions [90] are shown for comparison in Fig. 18. Clearly, the simulated results are in good agreement with the experiments. It can be seen that at a 0.9 keV incident energy and a normal incident angle, the energy distribution of the sputtered Ni atoms has a peak around 3 eV, but the energy of some emitted atoms extends to above 20 eV.

To show the effects of the ion incident energy and ion incident angle upon the energetics of the sputtered atoms, the average energy of the sputtered Ni atoms is plotted as a function of ion incident angle at the fixed incident energies of either 0.6 or 1 keV in Fig. 19(a). The average energy of the sputtered Ni atoms is shown as a function of ion incident energy at a fixed ion incident angle of 40° in Fig. 19(b). For the 0.6 keV ion incident energy, for instance, the average energy of the sputtered Ni atoms increased from about 12 eV to about 30 eV as the ion incident angle increased.
Fig. 18. Energy distribution of emitted nickel atoms following 0.9 keV Ar ion impacts with a [111] textured nickel surface.

from zero towards 70°. Further increases in incident ion angle result in a rapid drop of the energy of the sputtered Ni atoms. It is noted that at a low ion incident angle, impact can transfer high energy to the target crystal. On the other hand, the momentum of a high incident angle ion can be easily converted to a direction pointing out of the target surface during collisions. It is this trade-off between the energy transferred and the out of plane momentum created that results in the occurrence of maximum Ni energies at ion incident angles between 60 and 70°. Fig. 19 indicates that at an incident ion angle of 40°, the average energy of sputtered Ni atoms increases almost linearly as the incident ion energy is increased from 0.6 to 2 keV. Although the increase of the energy of the sputtered Ni atoms is not large, our results reveal that the sputtering yield increased from 3.34 to 5.99 atom/impact over the same ion energy range.

To examine the effects of the ion incident energy and ion incident angle upon the energetics of the reflected neutrals, the average energy of the reflected Ar neutrals is shown in Fig. 20 as a function of ion incident angle at the two incident energies of 0.6 and 1 keV. The average energy of the reflected Ar neutrals is plotted in Fig. 20(b) as a function of ion incident energy at a fixed ion incident angle of 40°. It can be seen that the average energy of the reflected Ar neutrals is almost zero at a normal ion incidence. The average energy of the reflected Ar neutrals increases rapidly with incident angle, and can approach the incident energy at large incident angles (70°). This is because at low incident angles, the ion transfers more of its energy to the target. At the fixed incident angle of 40°, the average energy of the reflected Ar neutrals ranges from about 50 eV at 0.6 keV ion incident energy to about 220 eV at 2
Fig. 19. The effects of (a) the ion incidence angle and (b) the ion energy upon the average energy of a sputtered nickel atom flux.
Fig. 20. The effects of (a) the ion incident angle and (b) the ion energy upon the average energy of a reflected neutral argon flux.
keV ion incident energy. The reflected neutrals retained about one tenth of their initial energy at this incident angle. Our calculations indicate that many of the reflected neutrals are propagated in a similar direction to the metal flux, and hence, are likely to strike the film during its growth.

5. Hyperthermal atom effects

The kinetic energy of atoms prior to their attachment to a growth surface varies from one deposition process to another. In MBE and electron beam deposition, the atoms are thermally evaporated and have low (thermal) energies \((kT \sim 0.1 \text{ eV})\). In high pressure sputter deposition (e.g. RF diode deposition), even though the atoms are ejected from their targets with energies in the 0.1–20 eV range, collisions with the background gas result in rapid thermalization. In low pressure magnetron sputtering, ion beam deposition and ionized sputter deposition, scattering is reduced and high energy species impact the growth surface. Fig. 21(a) show molecular dynamics simulations of the low energy (0.1 eV) deposition of copper (at normal incidence) followed by cobalt on a flat cobalt (111) surface at 300 K. The deposition rate was about 1 nm/ns. Fig. 21(b) shows the deposition of cobalt followed by copper on a flat (111) copper surface. Details of the computational procedures are given in Ref. [41]. A careful examination of the films shows that the cobalt on copper interface, Fig. 21(a) is not smooth, and several copper atoms have detached from the copper layer and are “alloyed” in the cobalt layer. The copper on cobalt interface in Fig. 21(b) is even less smooth, but the mixing of copper in cobalt and vice versa is absent.

The mechanisms responsible for these interfacial roughening and intermixing effects can be discovered by examining the time histories of atom coordinates during the simulation. This analysis indicates that under low energy deposition conditions (e.g. MBE or high pressure RF diode sputtering), atoms added to the structure attach at cradle sites very near to the impingement point of the atom with the surface [Fig. 22(a)]. If the deposition rate is high, or the lattice temperature is low, or if the activation energy for an atom to hop from one cradle site to another is large, the atoms are unable to diffuse to more tightly bound surface sites and a rough film develops. As a result, cobalt, with its higher melting temperature and higher diffusion activation energy develops a rougher surface than copper under low adatom energy deposition conditions. The mechanism for copper migration into an overlying cobalt layer is more subtle. When a rough cobalt surface is impacted by even a slow moving cobalt adatom, an atomic exchange can sometimes occur [Fig. 22(b)]. The process is more likely to happen when the copper atom that exchanges is less tightly bound to other copper atoms (i.e. when the surface is rough/defective) and is also sensitive to the relative binding energies of cobalt–cobalt, copper–copper, and cobalt–copper atom pairs. The net effect of exchange is that the copper atoms are propagated upwards through the first few monolayers of the cobalt film by repeated exchange events.

In deposition processes such as magnetron sputtering which operates at a low pressure (where thermalization by collisions with working gas atoms is less effective)
or in ionized physical vapor deposition where a weak bias voltage is used to electrostatically accelerate the depositing atoms, the deposited atoms can have impact energies in the 1–2 eV range. Fig. 21(c) and (d) shows MD simulations of deposition where all the arriving atoms have a 1.0 eV kinetic energy. Compared with thermal energy deposition, the interfaces that result from moderately hot atom condensation are smoother and exhibit less intermixing. The smoothing results from additional impact collision induced atomic reassembly shown schematically [Fig. 22(c) and (d)].

In some cases (where the impact atom makes near normal impact with the growth surface), the adatoms kinetic energy is transferred to atoms near the impact site, facilitating several atomic hops to sites of stronger binding. This form of “diffusion” is weakly dependent upon the equilibrium temperature of the substrate and has been termed athermal diffusion. In situations where an energetic atom makes a glancing local impact with the growth surface, the adatom can skip over the surface,
eventually arresting at a location some distance away from the impact site in the direction of initial incidence [Fig. 22(d)]. This has been called bias diffusion. It also depends weakly on the equilibrium temperature. The result is a smoother growth surface in which more atoms have complete coordination (stronger binding) and a reduced tendency for mixing when different atoms are deposited onto the growth surface.

Under very low pressure magnetron sputtering, ion beam deposition, or ionized sputter deposition with a large bias voltage, the atoms can have average energies of 5 eV or more. Fig. 21(e) and (f) shows the structure of multilayers grown with 5 eV metal atom impact energies. The interfaces are now quite flat because of the impact atom energy induced assembly processes described above. However, mixing, especially that of copper into the overlying cobalt layer, is greatly increased. This arises because the exchange mechanism increases in probability with the energy of the impacting atom. This trend overcomes the enhanced binding of the (on average) flatter surface.

The results above suggest that intermediate pressure sputtering processes, or those that use ionization and a bias voltage of around 1.0 eV are likely to result in the flattest, least intermixed interfaces. Indeed, the best GMR multilayer structures have been produced using intermediate energy (pressure) conditions with the magnetron sputter deposition method [91].
The mechanistic insights developed above suggest routes for the design of processes that might do better. For instance, increasing the impact energy (from say 0.1 eV) as the deposition of a layer progresses provides a means of both reducing the probability of the atomic exchange mechanism and flattening a growth surface during overgrowth of the next layer. Fig. 23(a) and (b) compares the effect of growth under only thermal conditions and a modulated atom energy scenario. In this case a low energy was used to deposit the first three monolayers of each new layer, followed by 5 eV for the remainder of the layer allows the growth of very flat unmixed interfaces. Practical processes for growing films in this manner have yet to be developed, but the simulations above suggest an approach that may have considerable merit for multilayers.

6. Ion assisted deposition

In ion beam deposition, energetically reflected neutrals with energies in the 100 eV range impact the growth surface. Inert gas ion beams with energies in the 50–500 eV range are also used to modify atomic assembly during ion assisted ion beam deposition.

![Diagram](image_url)

Fig. 23. Molecular dynamics simulations of modulated energy Co/Cu multilayer deposition.
deposition. Likewise, in diode sputtering, inert gas ions are accelerated across the substrate plasma sheath resulting in energetic (10–200 eV) impacts with the growing film. These impacts have been widely exploited to manipulate film growth and to control surface morphology, texture, grain size and stress.

Atomistic simulations can be used to access their importance for the growth of GMR multilayers. Again, it is possible to represent the inert gas neutrals (and ions) by a universal potential [86].

Fig. 24 shows a (111) copper crystal covered by a single monolayer of nickel (a) before and (b) after impacts by ten argon atoms with 50eV kinetic energy. It can be seen that seven copper atoms have exchanged lattice sites with nickel atoms due to the momentum (and energy) transferred by the impacting atoms. Numerous vacancies in the nickel layer were also formed. Increasing the energy of the impacting ions increases the probability of exchange (Fig. 25). For example, at 200 eV, almost three exchange events occur for each impact. Because the exchange mechanism is confined to atoms near the surface, increasing the thickness of the nickel overlayer rapidly reduces the exchange probability.

**Effect of High Energy Ar+ Ion Impact**

![Diagram](image)

**Fig. 24.** The effect of 50 eV argon bombardment upon a copper crystal covered by one monolayer (ML) of nickel.
The observations are significant. During RF diode and ion beam deposition the inert ion/reflected neutral fluxes are between 1/10 and 1/5 of the metal flux [61]. The impact energies depend upon process conditions but are usually in the 50–200 eV range. Assuming an average exchange probability of two per impact and a flux ratio of 1/5 imply that about 40% of the atoms in the first monolayer (ML) of nickel deposited on copper would be copper. About 40% of these would exchange with nickel atoms during deposition of the second nickel monolayer and so on. In addition, even when 2 ML of nickel cover the copper crystal, a few copper atoms in the top of the copper layer still suffer exchange. This results in an energetic ion/neutral induced copper concentration gradient in the nickel layer (even when no direct impact adatom exchange is likely, i.e. when the metal atoms are deposited with very low energies).

These results indicate that medium to high energy neutrals should be avoided in systems where mixing is likely. One way this can be done is to use low ion energies for sputtering in ion beam deposition. While this reduces the energy of the reflected neutrals, it also results in a reduced metal flux because of the reduced sputter yield. One way around this dilemma is to use heavier sputtering species. MD simulations of sputtering indicate that by using heavier xenon ions, the sputter yield at low ion energy is increased and the reflected neutral energy is reduced. For example, we find that a 500 eV argon impact at 45° to a (111) nickel surface results in reflected neutrals with an average energy of 54.5 eV. An identical xenon impact results in reflected neutrals with an average energy of 6.4 eV because of its more efficient energy transfer.

The results above also indicate that conventional ion assistance strategies using energetic (50–200 eV) inert gas ions are unlikely to improve the GMR ratio of metal
multilayers. Such conditions are encountered in ion assisted ion beam deposition and RF diode deposition under large power (or low pressure) conditions. While the layers are likely to be smoother, they will suffer appreciable intermixing.

However the results in Fig. 25 suggests that lower ion assistance energies might be of value. To explore this possibility, Fig. 26 shows MD simulations of low energy (0.1 eV) Cu/Ni/Cu deposition using very low energy normal incidence xenon atom assistance. They indicate that very low energy ion impacts do help to smooth the interfaces, but even 3 eV impacts with nickel on copper surfaces can cause atomic exchange. Modulating the assistance (Fig. 27) significantly reduces the mixing while enabling ion assisted flattening.

The origin of these flattening and mixing phenomena is the transfer of momentum from the assisting ion to metal atoms near the impact site. The efficiency of momentum transfer depends upon the masses of the inert gas and metal atoms involved in the impact. To evaluate this, MD simulations of inert gas atom assisted flattening can be conducted using a model surface like that shown in Fig. 28. This surface was then irradiated to a fluence of 0.5 atoms/Å² with various inert gas atoms. The fraction of cobalt atoms more than 1 ML above the copper surface was used as a roughness index and the number of cobalt atoms with more than three copper neighbors was used as an index of mixing. Fig. 29 shows that for each inert gas, an optimum energy exists where smoothing without mixing can be achieved. This optimum energy increases with reduction in the atomic mass of the assisting gas.

These results indicate that high fluxes of low energy inert gas ions can be used to manipulate the assembly of metal multilayers. This actuation process is in some ways preferable to the use of temperature, deposition rate, or the energy of the depositing atoms to mediate atomic assembly. It suggests that the use of thermal evaporation in conjunction with inert gas assistance is likely to produce films that are superior to those created by conventional RF diode or ion assisted ion beam deposition processes.

7. Surfactant mediated growth

The presence of very low partial pressures of background gases such as oxygen and water have been shown to significantly alter the resistance and magnetic properties of GMR multilayers [92,93–96]. Similarly it’s been shown that the deposition of very low levels of certain metals can also markedly affect the film composition and structure. Egelhoff et al. [92] for example, have shown that the magnetic properties of spin valves are dramatically improved when only a monolayer of lead was deposited in the chamber. Lead was thought to float out to the surface as deposition proceeded, thus continuing to promote smooth and coherent interfaces. The addition of Au was also found to promote smooth films [92]. Au, however, can alloy and may be left behind in the film, thus contributing to a reduction in the film’s magnetic properties.

While these additives and background gases are chemically quite different, they have both been described generally as “surfactants”. Understanding the mechanisms
\( \theta = 0^\circ \)
\( E_{\text{metal}} = 0.1\text{eV} \)
\( \text{Ion / metal} = 2 \)
\( T = 300\text{K} \)

(a) *No ion bombardment*

(b) \( E_{\text{Xe}} = 0.5\text{eV} \)

(c) \( E_{\text{Xe}} = 3.0\text{eV} \)

Fig. 26. MD simulations of Ni/Cu multilayer growth with constant very low energy xenon ion assistance.
\[ \theta = 0^\circ \]
\[ E_{\text{metal}} = 0.1 \text{eV} \]
\[ \text{Xe} / \text{metal} = 3 \]
\[ T = 300 \text{K} \]

(a) \( E_{\text{Xe}} = 0.5 \text{eV} \)

(b) \( E_{\text{Xe}} = 5.0 \text{eV} \)

Fig. 27. MD simulations of Ni/Cu multilayer growth with modulated low energy xenon ion assistance.

by which surfactants affect film growth is important because it may provide a new route to controlling thin film deposition processes and enable better atomic engineering of structure and therefore device properties. The mechanisms by which metal atoms and background gases control film growth, however, can be quite different due to the chemical properties of these additives.

Egelhoff's group at NIST has examined a wide range of different non metallic additives such as hydrogen, carbon, nitrogen, oxygen, CO and sulfur as well as metals including As, Ag, In, Sn, Sb, Te, Pb, and Bi by trial and error [92]. They
found various different effects. The most important and intriguing is that all of these helped to assist growth. Little, however, is known about how these species control growth kinetics. There have been a number of studies aimed at examining the role of surfactants in the epitaxial growth of various different films [92–118]. Much of the effort has been aimed at studies of metal atom surfactants such as Pb, As, Sb, Te, and In on the deposition and growth of Ag, Cu, and Co on well-defined Ag, Cu, and Pt surfaces. In addition, there have been a number of studies that have looked at the effects of As, Sb and Te on the deposition of Ge on Si. We have used first-principle quantum chemical calculations along with kinetic Monte Carlo and molecular dynamics in an effort to understand and model the mechanisms by which surfactants alter film growth and properties.

First principle density functional quantum chemical calculations were used to deduce the binding energies and mobilities of metallic and non-metallic surfactants on metal surfaces. The methods are the same as those described in Section 2.1.

7.1. Metal atoms

Consider the role of gold during the growth of Co/Cu films. Binding energies and diffusion barriers for Au and Cu on the Co(0001) and the (4×2) Co(0001) surfaces were determined for the same sites and diffusion paths analyzed in Section 2.1. The results are reported in Tables 1 and 2. The chemisorption energies for atomic Cu are nearly 1 eV lower than those for Co. The binding energies for Au are slightly lower than those for Cu. The weaker metal–metal bonding results in a significant lowering of the activation barriers for diffusion. The diffusion barriers for Cu along Co surfaces were found to be 0.081, 0.210 and 0.470 eV, respectively, for diffusion along the infinite terrace, along the bottom of the ledge, and away from the ledge on the bottom, in comparison to the 0.119, 0.519 and 0.840 eV for the diffusion of Co on
a) **Intermixing**

Fraction of mixed atoms to the total number of Co atoms

![Graph showing intermixing](image)

b) **Roughness**

Fraction of Co atoms remaining above first layer after 1500 ion bombardments

![Graph showing roughness](image)

Fig. 29. The effect of ion type and energy upon intermixing and surface roughness.
Co(0001). The barriers are decreased further if Au was used instead of Cu. The barriers for Au diffusion across the terrace, along the ledge and away from the terrace were calculated to be 0.105, 0.195 and 0.366 eV.

The results clearly show that the barriers of adatom diffusion for Au on Co(0001) are significantly lower than those for Co on Co(0001). Au can therefore act as an important surfactant if it can separate out to the top of the surface rather than alloying at the interface. More generally a comparison of the theoretical work presented here and the experimental findings by Egelhoff et al. [92] suggests that metals whose d-band is either filled or nearly filled interact more weakly on the surface. Adatoms which bind more weakly with the metal surface such as Au, Ag, and Pb have lower barriers for surface diffusion. As such they readily move across the surface and enable other atoms which deposit upon them to easily drop into the surface. They can thus act to “clean” the surface of assembly defects. Their surfactant effects however, also depend upon their resistance to being incorporated into the growing film.

Molecular dynamics simulations using the alloy potentials described in Section 2.2 can also be used to explore surfactant effects. Fig. 30 shows the MD simulated growth of two multilayers. In Fig. 30(a), a copper spacer layer was used. The Ni$_{75}$Co$_{25}$ on copper and copper on Ni$_{75}$Co$_{25}$ interfaces were both quite rough because of flux shadowing and limited adatom mobility. Fig. 30(b) shows a multilayer grown under identical conditions except that the copper layer contained 15% Ag, and 5% Au. A dramatically different interfacial structure results. Silver forms a highly mobile complex on the copper growth surface which promotes flattening. Its low solubility results in its continual rejection to the surface where it is most beneficial.

7.2. Background gases

Background gases such as oxygen and water exist in all but the lowest base pressure growth chambers and have been shown to significantly affect the film and its magnetic properties. Small amounts of oxygen, in even a UHV growth chamber, have been found to enhance GMR ratios and lower magnetic switching fields. However, the mechanism by which background gases cause these effects are quite different to the surfactant effects of metals. Molecular oxygen readily dissociates over Co leading to chemisorbed atomic oxygen. Atomic oxygen prefers the 3-fold fcc sites on Co(0001) where it binds at −5.0 eV. This is 1 eV stronger than the Co/Co(0001) bond strength. Because the Co–O bond is so strong, it is very unlikely that the diffusion of atomic oxygen enhances flattening. There are three alternative ideas, however, that have been proposed for other systems which may be important here as well. The Co–O bond is significantly stronger than the Co–Co bond. Therefore adsorption of oxygen on small 1–3 atom Co surface clusters may act to weaken the Co-surface bonds resulting in a small Co$_3$O cluster that can readily diffuse along the surface. This effect was shown by Beesenbacher and Norskov [119] who used the STM to track an isolated Pt atom and a Pt–H complex diffusing along the missing rows of a Pt (110) surface. The diffusion coefficient was greatly enhanced when
hydrogen was attached to a Pt adatom. This process can effectively be called “adsorbate-assisted diffusion”. The Co–O complex was found to lower the barrier to diffusion along the bottom ledge from 0.519 to 0.499 eV as shown in Fig. 31. The

Fig. 30. Molecular dynamics simulations of the growth of metal multilayers. In (a) a pure copper spacer layer was deposited. In (b) silver and gold were added to the copper layer. The silver acted as a surfactant and significantly increased the surface mobility. Gold had less effect and was retained in the copper layer. Both simulations were conducted at 300 K. The deposition rate was 1 nm/ns.
barrier for the diffusion of the Co–O complex away from the ledge was also found to be 0.077 eV lower than that for the Co atom diffusion. A second possibility for the enhanced film properties due to the presence of oxygen is that oxygen selectively pulls Co to Cu/Co interface. The Co–O bond energy was calculated to be 5.0 eV whereas the Cu–O bond energy is only 4.48 eV. The stronger Co–O bond will relax the surface in order to expose Co to the surface. Oxygen can therefore enrich the surface with cobalt. As Cu deposits onto the oxygen, oxygen can migrate out to the surface in order to avoid being trapped. It has been shown in the surface science literature that strongly bound adatoms such as oxygen will act to selectively pull one metal to the interface over another. We describe this process as surfactant-induced surface segregation.

A third plausible mechanism for the enhancement of the properties is that oxygen (or other gas) will adhere to specific adsorption sites which can impede or shutdown the growth from particular exposed facets.

We examined the “adsorbate-assisted surface cleaning” mechanism by performing DFT calculations on the diffusion of a simple Co–O complex on the Co(0001) and 4×2 Co(0001) surfaces. The results are shown in Table 2. The Co–Co(0001) binding energies for the Co–O complex on Co(0001) were found, in most cases, to be weaker than that for the atomic Co. The weaker Co–surface interactions lead to lower diffusion barriers. While this helps to support the effect of enhanced diffusion, the other mechanisms may also be active. These results lead to conclusions that surfac-
tant effects are almost certainly contributing to atomic assembly in real growth systems. A more detailed appreciation of their contribution may provide opportunities to manipulate the structure of vapor deposited materials.

8. Summary

The beginning of a reliable framework for analyzing the fundamental mechanisms of atomic and molecular assembly during the growth of thin films is emerging. It exploits advances in ab-initio computation of structure, molecular dynamics simulations (aided by new potentials) of structure evolution and kinetic Monte Carlo techniques to develop a detailed understanding of the key processes and their sensitivity to process conditions. Significant progress appears possible by coupling this capability with more continuum approaches to the analysis of microstructure evolution.

The early stage modeling tools available today are beginning to find widespread use for simulating film growth processes. In the case of GMR multilayer growth, they have identified promising new directions for process development. In particular, processes that enable control of adatom and assisting ion fluxes in the 1–20 eV region promise to enable the growth of exceptionally smooth, relatively unmixed interfaces. As the capabilities of these modeling approaches are advanced, it is likely that modeling can be applied to many more of the complex nanoscale systems shown in Fig. 1.

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