Review on Phase-field Simulation on PVD

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ABSTRACT

This article briefly reviews recent applications of the phase-field method on PVD of thin films. It starts with a brief introduction to the phase-field method and the Physical Vapor Deposition. The solution of the partial differential equations yields the temporal evolution of the phase-field variables are presented, including the Ginzburg–Landau equation and Cahn–Hilliard equation, then introduces the free energy functional and historical evolution of phase-field method. Thin films are usually grown using physical vapor deposition (PVD) techniques, where the precise deposition conditions and materials used strongly influence the surface morphology and underlying microstructure that arises during processing. Computational methods are often used in conjunction with experimental observations due to the many complicated and nonlinear evolution processes. Development of the phase-field method has provided a simple yet powerful tool for simulating and studying many materials evolution processes. As such, the phase field method provides a unique and versatile technique for investigating the effects of PVD conditions on thin film microstructure formation and evolution.

INTRODUCTION

Phase-Field Method And Its Historical Evolution

More than a century ago, van der Waals [2] already modeled a liquid–gas system by means of a density function that varies continuously at the liquid–gas interface. Approximately 50 years ago, Ginzburg and Landau[3] formulated a model for superconductivity using a complex valued order parameter and its gradients, and Cahn and Hilliard[1] proposed a thermodynamic formulation that accounts for the
Gradients in thermodynamic properties in heterogeneous systems with diffuse interfaces. The stochastic theory of critical dynamics of phase transformations from Hohenberg and Halperin [4] and Gunton et al. [5] also results in equations that are very similar to the current phase-field equations. Nevertheless, the concept of diffuse interfaces was introduced into microstructural modeling only 20 years ago. There are essentially two types of phase-field model that have been developed independently by two communities.

The first type of phase-field model was derived by Chen [6] and Wang [6, 7] from the microscopic theory of Khachaturyan [5, 8]. The phase-field variables are related to microscopic parameters, such as the local composition and long-range order parameter fields reflecting crystal symmetry relations between coexisting phases. The model has been applied to a variety of solid-state phase transformations (see [9] for an overview) that involve a symmetry reduction, for example the precipitation of an ordered intermetallic phase from a disordered matrix [10-12] and martensitic transformations [13, 14]. It was also applied to ferroelectric [14, 15] and magnetic domain evolution [16] and can account for the influence of elastic strain energy on the evolution of the microstructure. In the second type of phase-field model, a phenomenological phase-field is used purely to avoid tracking the interface. The idea was introduced by Langer [17] based on one of the stochastic models of Hohenberg and Halperin [4]. The model is mainly applied to solidification, for example to study the growth of complex dendrite morphologies, the microsegregation of solute elements and the coupled growth in eutectic solidification (see [18, 19] for an overview).

Recently a new continuum modeling approach, the phase-field crystal model, was introduced [20-23]. It allows us to simulate microstructural behavior on atomistic length scales and diffusive time scales. Hence, the spatial resolution is of the same order as for molecular dynamics simulations; however, it is possible to consider much longer time scales. In the phase-field crystal model, the phase-field variable is the local atom density. For solid structures the free energy is minimal for periodic solutions of the density field, whereas in the liquid it is minimal for a constant value of the density field. Due to the periodicity of the density field and the atomic resolution, crystal anisotropy and the interaction between elastic lattice deformations, dislocation movement and plastic deformation [24] are incorporated automatically. Moreover, the diffuse-interface related problems of phase-field models are avoided. Up to now simulations have only been for two-dimensional systems and simple crystal structures. The possibilities of the technique are still to be explored further and efficient numerical techniques that exploit the periodicity of the solution have to be developed.

The phase-field method is a simulation technique commonly used to numerically model materials microstructure evolution processes. The phase-field method originated with the Landau mean field theory of phase transformations, where an order parameter (i.e., a field variable) is introduced to describe a phase transformation [25]. This order parameter reflects the spatial configuration of the
entire system being considered and is therefore spatially dependent. The order parameter for a system is treated as an average thermodynamic quantity that is used to determine the free energy of the system, which can then be used to calculate thermodynamic properties of the system. However, in the construction of the free energy in the Landau mean field theory, no consideration was given to the existence of interfaces between phases, whose presence, migration, and interactions are fundamental aspects governing microstructure formation and evolution in materials[25]. A simple expression for a free energy functional is given in Equation 1[9].

$$F = \int \left( f(c_1, \cdots, c_n, \eta_1 \cdots \eta_{1p}) + \sum_{i=1}^{n} \alpha_i (\nabla c_i)^2 + \sum_{i,j=1}^{p} \beta_{ij} \nabla \eta_i \nabla \eta_j \right) d\Omega \quad (1)$$

Here, $f$ is the local free-energy density. The function, $f$, also provides an energetic barrier between the stable and/or metastable phases that are present. The second and third terms in Equation 1, which are gradients of the field variables, capture interfacial energy contributions that arise from compositional or structural changes, respectively. The interfacial gradient coefficients, $\alpha_i$ and $\beta_{ij}$, are related to interfacial thicknesses and energies, which in general may be anisotropic[9, 25, 26].

With a physically relevant free energy functional constructed, the spatial and temporal evolution of the field variables, and thus the physical quantities, is obtained by solving either the Allen-Cahn expression in Equation 2 or the Cahn-Hilliard expression in Equation 3, depending on the physical processes to be modeled. These equations describe the evolutionary dynamics of non-conserved and conserved quantities, respectively[9, 25].

$$\frac{\partial \eta_i(r,t)}{\partial t} = -M_{pq} \frac{\delta F}{\delta \eta_q(r,t)} \quad (2)$$

$$\frac{\partial c_i(r,t)}{\partial t} = \nabla \cdot \left( M_{ij} \frac{\delta F}{\delta c_j(r,t)} \right) \quad (3)$$

Here, $M$ are kinetic coefficients that can be related to atomic or interfacial mobilities and the $\delta F$ terms represent the functional derivatives of the free energy functional with respect to the appropriate field variable[9, 25, 26].

**Two Important Phase-Field Equations**

**TIME-DEPENDENT GINZBURG-LANDAU EQUATION**

The non-conserved variables $\eta_k(r,t)$ and $\phi_k(r,t)$ govern a time-dependent Ginzburg–Landau equation, also referred to as a Allen–Cahn equation. For the order parameter field representation,

$$\frac{\partial \eta_k(r,t)}{\partial t} = -L_k \frac{\delta F}{\delta \eta_k(r,t)} = -L_k \left[ \frac{\partial f_0}{\partial \eta_k} - \nabla \cdot k_k \cdot \nabla \eta_k \right] \quad (4)$$
Which is obtained for $k = 1 \cdots p$, $L_k$ and $k_k$ may depend on the local values of the field variables to introduce anisotropy or composition dependence of the interfacial energy or mobility.

In the single-phase-field model, the evolution of $\phi$ is given by

$$
\frac{\partial \eta_k(r,t)}{\partial t} = -L_k \frac{\delta F(x_B, \phi)}{\delta \phi(r,t)} = -L \left[ \frac{\delta F(x_B, \phi)}{\delta \phi} - \nabla \cdot k(\phi) \cdot \nabla \phi \right]
$$

(5)

Where it is assumed that $k$ may depend on the phase-field. In the multiphase-field model, the technique of the $\lambda$-multiplier is applied to account for restriction on every position in the system:

$$
\frac{\partial \phi_k(r,t)}{\partial t} = -L \frac{\delta F'(x_B, \phi_l)}{\delta \phi_k(r,t)}
$$

(6)

$$
F' = \int [f(x_B, \phi_l, T^*) + \lambda (\sum_{l=1}^{p} \phi_l - 1)] dv = F + \int [\lambda (\sum_{l=1}^{p} \phi_l - 1)] dv
$$

(7)

and $F'$ and $f(x_B, \phi_l, T^*)$ respectively the total free energy and the free energy density. Elimination of $\lambda$ gives

$$
\frac{\partial \phi_k(r,t)}{\partial t} = -\frac{1}{p} \sum_{l=1}^{p} \left( \frac{\delta F}{\delta \phi_k(r,t)} - \frac{\delta F}{\delta \phi_l(r,t)} \right)
$$

(8)

with $p$ the number of phase-fields. The $L$ and $L_k$ are positive kinetic parameters, related to the interfacial mobility $\mu$. It was calculated by Allen and Cahn[27], assuming that $\frac{1}{\rho} \ll 1$ with $1/\rho$ the local curvature of the interface and $l$ the interfacial thickness, that the interfacial velocity equals.

$$
\nu = L_k \left( \frac{1}{\rho} \right)
$$

(9)

For curvature driven coarsening of the anti-phase domain structure. In classical sharp-interface theories for curvature driven motion of interfaces, the velocity of an interface is given by

$$
\nu = \mu \sigma_{int} \left( \frac{1}{\rho} \right) = \mu^* \left( \frac{1}{\rho} \right)
$$

(10)

Where $\mu$ is called mobility and $\mu^*$ reduced mobility. Analogous to the anisotropy in interfacial energy, anisotropy in interfacial mobility is introduced by giving $L$ a dependence on the interfacial orientation through the angle $\theta$. 

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CAHN-HILLIARD EQUATION

The evolution of conservative phase-field variables, such as the molar fraction field \(x_B(r,t)\), obeys a Cahn–Hilliard equation, for example,

\[
\frac{1}{V_m} \frac{\partial x_B(r,t)}{\partial t} = \nabla \cdot M \nabla \frac{\delta F(x_B,\eta_k)}{\delta x_B(r,t)} = \nabla \cdot M \nabla \left[ \frac{\partial f_0(x_B,\eta_k)}{\partial x_B} - \nabla \cdot \nabla x_B(r,t) \right]
\] (11)

The kinetic parameter \(M\) can be a function of the order parameter fields and the composition. The Cahn–Hilliard equation is essentially a diffusion equation of the form

\[
\frac{1}{V_m} \frac{\partial x_B(r,t)}{\partial t} = -\nabla \cdot J_B
\] (12)

Where the diffusion flux \(J_B\) is given by

\[
J_B = -M \nabla \frac{\delta F}{\delta x_B} = -M \nabla \left[ \frac{\partial f_0(x_B,\eta_k)}{\partial x_B} - \nabla \cdot \nabla x_B(r,t) \right]
\] (13)

Mass conservation is accordingly ensured, as well as the flux balance at the interfaces. The diffusion fluxes are defined in a number fixed reference frame (the number of moles per unit volume in the number fixed reference frame, is constant in time) and the parameter \(M\) relates to the inter diffusion coefficient \(D\) as

\[
M = \frac{V_mD}{\partial^2 G_m/\partial x_B^2}
\] (14)

Which gives for an ideal solution

\[
M = \frac{Dx_B V_m}{RT}
\] (15)

\(M\) can also be expressed as a function of the atomic mobilities of the constituting elements \(M_A\) and \(M_B\)

\[
M = \left( \frac{1}{V_m} \right) x_B (1 - x_B) [x_B M_A + (1 - x_B) M_B]
\] (16)

Atomic mobilities are related to tracer diffusion coefficients. If sufficient experimental information is available, expressions for the temperature and composition dependence of the atomic mobilities \(M_i\) can be determined using the DICTRA (Diffusion Controlled Transformation) software. To account for differences in diffusion properties between the coexisting phases and for enhanced grain boundary diffusion, \(M\) may depend on the order parameter fields or phase-fields.
Physical Vapor Deposition and Free Energy Functional

PVD is a vapor deposition technique in which atoms are evaporated or sputtered from a target material source. These ejected atoms then travel through the deposition chamber and condense into a solid as a coating on a substrate. The working principle of the PVD growth process schematic representation in Figure 1[9, 25, 28].

The PVD process is performed in a vacuum or a very low-pressure environment with an inert or active atmosphere (i.e., an B vapor phase could react with an N atmosphere to produce the compound, e.g., cBN). The low pressures used in PVD significantly reduce the number of gas-phase reactions and collisions during vapor transport, thus allowing physical processes to dominate.

![Figure 1. Schematic representation of the PVD growth process.](image)

The novel PVD model has developed in recent years, it is a straightforward extension of the Keblinski et al.[28, 29] PVD model described by incorporating grain orientation and grain boundary(GB) effects in the manner proposed by Warren et al.[30]. This extension allows for the modeling and simulation of simultaneous solid growth, surface feature formation, grain growth, and GB migration under PVD conditions, which is an improvement on the sequential method developed. Using the variables $f(r, t)$ and $\theta(r, t)$, this extension is contained within the free energy functional shown below in Equation 4.

$$F = \int \left( -\frac{1}{2} f^2 + \frac{1}{4} f^4 + a(\nabla f)^2 + s \frac{\ell +1}{2} \left| \nabla \theta \right| + \frac{\varepsilon^2}{2} \frac{(\ell +1)^2}{2} \left| \nabla \theta \right|^2 \right) d\Omega$$

(17)
While, to model PVD within the phase-field framework, the model introduces two field variables: \( f(r, t) \) and \( g(r, t) \). The first field variable, \( f(r, t) \), describes the growing thin film solid where \( f(r, t) \approx 1 \) defines a solid region, \( f(r, t) \approx -1 \) defines a region of vacuum or no solid while \( \theta(r, t) \) describes the local grain orientation as measured from a defined global axis (the positive x-axis in Warren et al.\([30]\), and \( f(r, t) \approx 0 \) naturally defines the solid-vapor interface. The second variable, \( g(r, t) \), describes the density of the incident vapor flux where \( g(r, t) \approx 0 \) defines a region of no vapor flux and \( g(r, t) > 0 \) defines the local density of incident vapor being transported to the thin film surface. Furthermore, the grain gradient coefficient functions are taken to be quadratic in the local solid density \( f_s(r, t) = (f(r, t) + 1)/2 \) so that orientation effects are removed within the disordered vapor region as there is no physical meaning of order within this region.

With this free energy functional containing variables to describe solid and grain evolution, all equations of motion for PVD of a single-phase polycrystalline material can then be determined. The complete set of equations used in this research is shown in Equations 5, 6, and 7. Equations 5 and 6, which are the equations of motion proposed by Keblinski et al.\([16]\), are used here to describe all PVD growth processes for the solid phase. The inclusion of the orientation parameter, \( \theta(r, t) \), requires an additional equation of motion describing its evolution. This is determined from Allen-Cahn dynamics (Equation 2) and gives rise to the grain equation of motion in Equation 7.\([28]\]

\[
\frac{\partial f}{\partial t} = \nabla^2 f + B(\nabla f)^2 g + C(\nabla f)^2 g \eta \quad (18)
\]

\[
\frac{\partial g}{\partial t} = \nabla[DG - Ag] - B(\nabla f)^2 g \quad (19)
\]

\[
P(|\nabla \theta|) \tau_\theta \left( \frac{f + 1}{2} \right)^2 \frac{\partial \theta}{\partial t} = \nabla \cdot \left[ \left( \frac{f + 1}{2} \right)^2 \left( \frac{s}{|\theta|} + \varepsilon^2 \right) \nabla \theta \right] \quad (20)
\]

**CONCLUSIONS**

This article gives a review to the phase-field method on PVD and an overview of its possibilities. The phase-field method is a versatile and powerful technique for simulating microstructural evolution with PVD, which is currently very popular. Amongst others, it has been applied to solidification, precipitate growth and coarsening, martensitic transformations and grain growth and, more recently, also to other solid-state phase transformations like the austenite to ferrite transformation in steels, dislocation dynamics, crack propagation and nucleation. The achievements are increasing rapidly due to improved modeling and implementation techniques and growing computer capacities.

In the phase-field method of PVD, a microstructure is represented by means of a set of conserved and non-conserved phase-field variables that are continuous...
functions of spatial coordinates and time. The molar fraction fields of the constituting components are typical examples of a conserved phase field variable. Non-conserved phase-field variables, such as order parameter fields and phase-fields, contain information on the local structure and orientation. Within domains the phase-field variables have nearly constant values, and at the interface they vary continuously over a narrow region between their values in the neighboring domains. Consequently, the interfaces have a finite width and the variations in properties at interfaces are continuous. This is called a diffuse-interface description. The main advantage of diffuse interfaces is that no boundary conditions must be specified at the moving interfaces. Therefore, phase-field models are able to predict complex morphological evolutions. Furthermore, no a priori assumptions on the (non-)equilibrium conditions at the moving interfaces are required.

Phase-field models contain a large number of phenomenological parameters, which have to be determined in order to obtain quantitative results for real material. The parameters are related to the thermodynamic properties and equilibrium composition of the coexisting phases, the interfacial energy, width and mobility, the diffusion properties of the solute elements, and the elastic properties of all coexisting phases. Due to the large number of parameters and because some of them are related to properties that are difficult to measure, it is complicated to determine all the parameters in a phase-field model. Different methodologies have been proposed to make parameter assessment more efficient and to reduce the dependence on experimental measurements. Moreover, atomistic simulations can provide information on difficult-to-measure properties, such as the interfacial energy and mobility and their anisotropy. However, parameter assessment is still a major problem in phase-field modeling.

The numerical solution and implementation of phase-field equations is, in principle, relatively simple and straightforward, as there is no need to track the interfaces. However, the resolution of the numerical technique must be very fine to catch the steep transitions of the phase-field variables at interfaces. Simulations for realistic system sizes and time scales are therefore not feasible using the ordinary numerical techniques, because of excessive computation times and insufficient computer memory. A finite volume or finite element discretization using an adaptive mesh is often applied for simulating crystal growth in solidification. Then, the mesh is taken extremely fine at the gas-solid interface, to resolve the transition of the phase-field variables, and coarse within the bulk domains, for describing the mass and heat transfer over macroscopic distances.

To increase the system size towards relevant dimensions, the width of the diffuse interface must be taken artificially large. Therefore, it is important to develop phase-field formulations that allow us to change the interface width without affecting the interfacial energy and mobility or introducing spurious effects. A lot of progress has been made in controlling the interfacial profiles of the phase-field variables and suppressing artificial kinetic and non-equilibrium effects, although a general solution has not yet been found and all strategies are still under debate.
ACKNOWLEDGEMENTS

Project supported by National Natural Science Foundation of China (Grant No. 51765001 andGrant No. 11764002 ), National Natural Science Foundation of Ningxia, China (Grant No. NZ15103).

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