Nano-scale Material by Design

D. Bleau[*], E. Eisenbraun[**] and J. Raynolds[**]

[*]Benet Laboratories, Watervliet Arsenal
[**]College of Nanoscale Science and Engineering, University at Albany,
State University of New York, Albany, NY 12203

ABSTRACT

This research is aimed at developing a fundamental understanding of how atomic scale processing and nano-scale film performance characteristics can be predictably correlated by the use of kinetic Monte Carlo and phase-field simulations of PACVD processes. Our modeling builds on previous approaches in the use of first-principles density functional calculations to provide important thermodynamic and kinetic information to Monte Carlo and phase field simulations. By combining these approaches we will be utilizing a multi-scale modeling paradigm to bridge the length and time scales from the nanometer/nanosecond regime up to the macro (reactor-scale) realm. This work ultimately has direct applications toward cross-disciplinary functional capabilities in areas including propulsion, energy conservation, medical components, and nanoelectronics.

Keywords: CVD modeling, phase field, density functional theory, SiCN

1 INTRODUCTION

This report presents an overview of a joint theoretical/experimental collaboration aimed at the development of high performance thin-film coatings for a wide variety of protective coating applications. The desired properties of such coatings include high hardness, high thermal conductivity, high melting temperature as well as good mechanical stability. We have chosen to focus our efforts on the development of SiCN thin-films grown using plasma-assisted chemical vapor deposition (PACVD) processing. We seek to develop a detailed fundamental understanding of the connection between processing parameters (composition, temperature, etc) and the properties of the resulting thin film. The first part of this report is an overview of efforts aimed at the development of a predictive, fundamental theoretical understanding followed by a discussion of our experimental approach and recent progress.

2 THEORETICAL APPROACH

2.1 Modeling the growing surface

Two promising approaches have been introduced in recent years to model the detailed interplay between thermodynamic and kinetic influences occurring in thin-film growth: kinetic Monte Carlo (KMC) [1] and Phase-Field techniques [2].

2.2 Kinetic Monte Carlo vs. molecular dynamics

The KMC approach is an atomistic approach in which all relevant local chemical reactions at the growing surfaces are simulated to determine the composition and morphology of the growing surface vs. processing parameters. This approach has recently been successfully applied to the problem of CVD growth of diamond thin films [3].

Another approach that attempts to accurately treat the detailed chemical interactions at the growing surface employs the use of molecular dynamics (MD) simulations. In a molecular dynamics simulation, Newton's equations of motion are solved at each time step for an ensemble of atoms characterizing the growing surface. Unfortunately, however, in this approach one is drastically limited to very short time scales for the overall simulation. This is because of the fact that in a molecular dynamics simulation, the time step must be kept very small in order to correctly integrate the equations of motion governing very fast reactions. In the problem that we face (CVD deposition of thin films) there are chemical reactions occurring on varying time scales from very short to very long (reaction rates differ by orders of magnitude). The MD approach is therefore unsuitable for our purposes.

The KMC approach has the advantage that chemical reactions occurring at all time scales are correctly incorporated. This happens because, unlike in a MD simulation, the time step in a KMC calculation is not limited by the fastest occurring reaction. At each time step, a random number is generated, and based on this number, a reaction is chosen according to it probability of occurring during that time step. This probability is proportional to the reaction frequency. Thus over many times steps, fast reactions will have dominated the growth process (as is expected in the actual process) however slow reactions also take place.

One key drawback of the KMC approach, however, is the need to characterize all possible chemical reactions that can occur at the growing interface. In the case of diamond growth, the surface chemistry was well characterized. The

input to these simulations was a list of dozens of possible reactions and corresponding kinetic data (free energy differences and rate constants for each reaction) [3]. For the case of SiCN, unfortunately, the details of the surface chemistry considerably less well known. Therefore, one of the goals of the present work, is the study of the detailed chemical reactions occurring at the surface using quantum chemical techniques as will be described in a following subsection.

2.3 Phase-field modeling

In contrast to KMC, phase-field modeling is a continuum approach that describes the morphology and composition profiles of the growing surface in terms of continuous fields. In this approach, one begins with a free-energy functional that, in the simplest case, depends on two fields, the composition u and the phase field ϕ. For a two-component system, for example solid and liquid, the phase field satisfies $-1 \le \phi \le 1$, taking on one value (e.g. -1 in the solid) in the one phase and the other (e.g 1 in the liquid). The interface between the two phases corresponds to localized regions in which the phases field varies between these two values.

As a simple example, we consider the generic free energy functional for a two-component system, which is written [4] as:

$$F[\phi, u] = F_1[u] + F_2[\phi] + F_{\text{int}}[\phi, u], \qquad (1)$$

where, the first and second terms depend on the respective fields u and ϕ separately, and the third term accounts or the mutual interaction of these fields. The third term would naturally account for the possibility that the phase field could depend on the composition (i.e. composition dependence of phase transitions).

Equations of motion for the composition and phase fields, u and ϕ, are obtained through minimization of the free-energy functional given in Eq. 1. These are:

$$\frac{\partial u}{\partial t} = \nabla \bullet \left[M(\phi, u) \nabla \frac{\delta F}{\delta u} \right], \qquad (2)$$

and,

$$\frac{\partial \phi}{\partial t} = -\gamma(\phi, u) \frac{\delta F}{\delta \phi} = -\gamma(\phi, u) \left[\frac{\delta F_2}{\delta \phi} + \frac{\delta F_{\text{int}}}{\delta \phi} \right]. \qquad (3)$$

Equation (2) is of the Cahn-Hilliard form for the conserved composition field u, while Eq. (3), for the non-conserved phase field ϕ is of the Allen-Cahn form [4]. The mobility coefficients M and γ, in general, depend on the phase field and the composition. The analytic forms for

M and γ depend on the specific form chosen for the free energy functional $F[\phi, u]$ as discussed in Ref. [4].

Notable recent applications of phase-field techniques to surface growth include: (1) a study of spiral surface growth (spiral steps nucleating at a dislocation) [5] and, (2) the development of free-energy functionals giving rise to atomic scale density modulations including effects of strain energies associated with grain boundaries [6].

2.4 Solution of the phase field equations: finite elements

We are developing a phase field approach to CVD growth of SiCN thin films. The equations analogous to Eqs. (2) and (3) will be solved for two and three dimensions using finite-element techniques embodied in the commercial software package FEMLAB. The results of such calculations will be compared with experimental results to assess the accuracy of the model parameters. Through such comparisons and further input from quantum chemical calculations, the model will be refined.

2.5 Fundamental input from quantum calculations: density functional theory

An important component of this research is the use of first-principles calculations, based on the Density Functional Theory (DFT) to provide input for KMC and phase field models. As discussed previously, KMC requires kinetic data regarding chemical reactions occurring at the growing surface. In particular we need (free-) energy differences as well as reaction barriers. Such information is being determined from density functional calculations. In particular we employ the Generalized Gradient Approximation (GGA), which is known to improve the description of reaction barriers.

Two different methods are being employed for DFT calculations: (1) VASP [7] and (2) Abinit [8]. Both computer codes are implementations of DFT within a plane-wave/pseudopotential basis and they have complementary capabilities. VASP for example, is extremely computationally efficient but has relatively limited capabilities as compared to Abinit. Abinit, on the other hand, has an extraordinary array of properties that can be calculated at the price of being far less efficient.

In addition to providing chemical reaction data for KMC, first-principles calculations are being employed to determine free-energy functionals for use in the phase-field method. The current state of the art allows the calculation of compositional phase diagrams based solely on input from first-principles calculations [8]. Composition and thermal free energies can be calculated as well as strain-dependent free energies. Other important information includes: (1) lattice and elastic constants, (2) thermal expansion coefficients, (3) interfacial free energies, etc.

As an example, we consider the calculation of thermal free energies for a specified composition. The primary

ingredient for such a calculation is the detailed spectrum of lattice vibrations (phonons). Using self-consistent Density Functional Perturbation Theory (DFPT) it is now possible to calculate the full phonon spectrum of relatively simple (i.e. fairly small unit cells) materials [9]. Such a calculation, obtained from Abinit, is shown in Fig. 1 for Si.

The temperature-dependent thermal free energy is obtained by carrying out a certain integral over the allowed phonon states. Also, by considering strain-induced changes in the phonon spectrum we obtain thermal expansion coefficients. Thermal conductivities are also obtained by considering non-linear interactions of phonons that are also obtainable through the use of DFPT as implemented in Abinit. In addition to the phonon spectrum we also obtain, as a byproduct, the electron-phonon interaction matrix elements. Such information is important to understanding electronic transport properties.
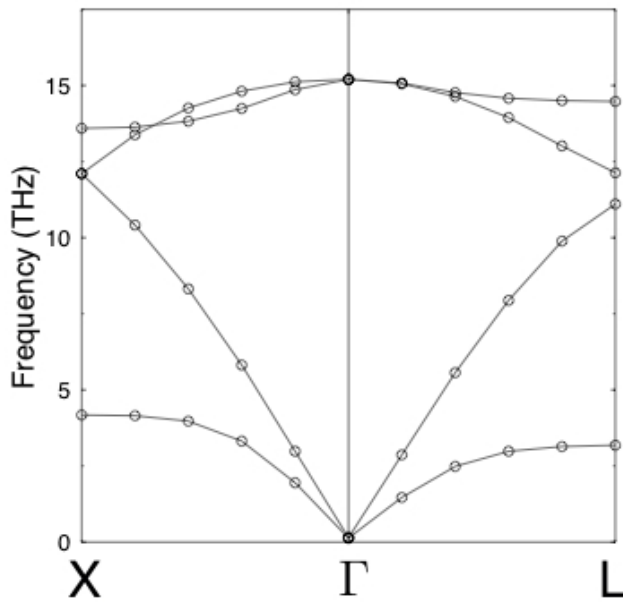

Figure 1: Calculated phonon band structure for Si. This calculation was carried out using the Abinit code and is based on DFPT.

To emphasize the importance of first-principles calculations of free-energies, we note that such calculations are completely parameter free and require no experimental input. The only input is description of the system in terms of the location of a collection of atoms in a representative unit cell along with the corresponding atomic numbers. Using such techniques allows us to make predictions of free energies vs. composition, temperature, and strain as is needed as input for the phase-field simulations.

The downside of using first-principles methods is the extreme demand on computational resources that is typically required. This results from the fact that such methods typically scale as the cube of the number of atoms

in the system. Therefore we are forced to make approximations for large systems based on results obtained for small systems.

As an example, consider the computation of thermal expansion coefficients. For an ordered, periodic solid such as cubic SiC we can obtain accurate results from calculations of the phonon band structure (similar to that shown in Fig. 1). However, the material we wish to consider, SiCN is amorphous and requires a large unit cell for its proper description. For such a material, a complete calculation of the phonon band structure from DFPT would be prohibitively expensive. We can, however, obtain a reasonable approximation based on the non-linearity of the energy vs. volume relation.

The energy vs. volume relation for cubic SiC, based on a VASP calculation is illustrated in Fig. 2. From this curve we obtain the lattice constant, bulk modulus, and thermal expansion coefficient. This simple technique will be employed for large unit cells required to correctly describe amorphous structures.
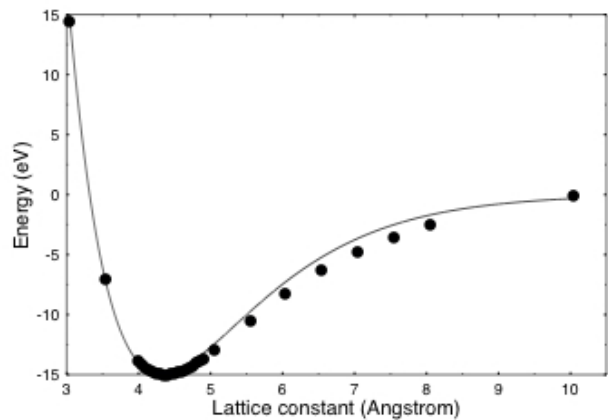

Figure 2: Plot of total energy vs. lattice constant for cubic SiC (calculated with VASP). Such curves will be calculated for large unit cells (describing amorphous structures) and used to obtain the lattice constant, bulk modulus, and thermal expansion coefficients.

2.6 Summary of theoretical approaches

We are pursuing a multi-scale modeling approach combining the use of Density Functional Theory, Kinetic Monte Carlo and phase field techniques to describe the CVD growth of SiCN thin films. The two modeling approaches (KMC) and phase-field methods yield similar information: the composition profile and morphology of the growing surface vs. processing parameters. The KMC approach, however, requires detailed information regarding plausible chemical reactions and their corresponding kinetic

data. The resulting surface profile gives atomistic-level resolution.

The phase-field method is a continuum approach based on a free-energy functional. The phase-field model approach has the advantage that it is more easily implemented and solved using finite-element techniques. It also requires less information as input to the construction of the free-energy functional.

Calculations based on DFT are being carried out to provide input to both modeling approaches.

3   EXPERIMENTAL APPROACH AND PRELIMINARY RESULTS

In order to develop a complete solution for material development by design, a plasma-assisted chemical vapor deposition (PACVD) process was developed to enable the growth of SiCN nanoscale coatings with modulated composition. In particular, this process was developed so as to allow controllable, repeatable Si:C:N ratios via simple, reversible changes to the processing conditions. This work was carried out using a modified Varian MB^2 200-mm wafer cluster tool. The PACVD process employs 2,4,6-trimethyl-2,4,6-trisila-heptane as the Si and C source, and a mixture of H_2 and N_2 as co-reactants in a 13.56MHz plasma environment, to both bind up residual precursor fragments and to provide a source of nitrogen to the system. Precursor flow was fixed at 50sccm employing an MKS Instruments type 1153 vapor source mass flow controller and H_2/N_2 flows were varied between 50 and 1000 sccm employing MKS type 1179 mass flow controllers. The wafer temperature was 300°C, and the plasma power was held at 100W. Process pressure was 1 torr.

It was found that film composition could be easily modulated by varying the process parameters as described above. Figure 3 plots the composition as a function of H_2/N_2 flow ratio in the PACVD process as measure by Auger electron spectroscopy (AES). As can be seen, as the relative partial pressure of N in the process increases, the concentration of N in the films increases, at the expense of Si and C concentration, which generally decrease over the range investigated.

It can also be observed that the oxygen incorporation in the films varies over the processing regime investigated. Specifically, the amount of O in the films increases at both low and high H/N ratios. It is suggested that this is due to a lower specific film density or higher porosity at these extreme conditions, thus allowing O from ambient exposure to penetrate into the film matrix (since there is no O in the Si-C precursor material). It is expected that the degree of O incorporation will be related to the mechanical properties of the SiCN film.

These samples are currently undergoing mechanical performance testing, and the results will be compared with those predicted by our modeling and simulation approaches. Based on these results, a model will be developed to capture the relationship between processing

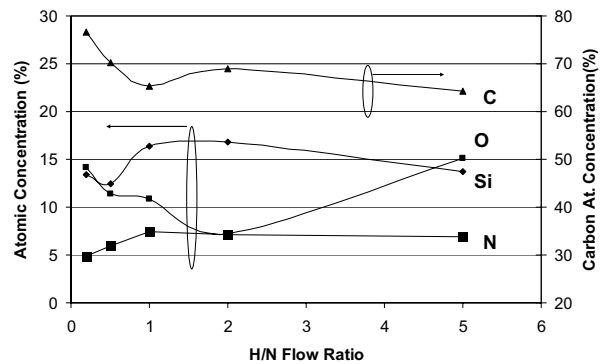conditions, film composition, and subsequent mechanical properties.

Figure 3: PACVD SiCN composition as a function of gas flow ratio as measured by Auger electron spectroscopy. N concentration can be controlled by altering the N flow. Note that carbon composition is plotted on the right axis for clarity, and the trend lines are included as a guide.

REFERENCES

[1] C. C. Battaile, and D. J. Srolovitz, Annu. Rev. Mater. Res. **32**, 297 (2002)

[2] W. Boettinger, J. A. Warren, C. Beckermann, and A. Karma. Ann. Rev. Mater. Res. **32**, 163 (2002).

[3] C. C. Battaile, D. J. Srolovitz, and J. E. Butler, J. Crystal Growth, **194**, 353 (1998).

[4] J. W. Cahn, P. Fife, and O. Penrose, Acta. mater. **45**, 4397 (1997).

[5] A. Karma and M. Plapp, Phys. Rev. Lett. **81**, 4444 (1998).

[6] K. R. Elder, M. Katakowski, M. Haataja, and M. Grant, Phys. Rev. Lett. **88**, 245701 (2002).

[7] G. Kresse, and J. Furthmueller, Phys. Rev. B **54**, 11169 (1996).

[8] *The abinit software project:* www.abinit.org.

[9] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001). (see also references within).