Hierarchical simulation of microcrystalline PECVD silicon thin film growth and structure

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We have designed and implemented a hierarchical simulation methodology capable of addressing the growth rate and microstructural features of thin silicon films deposited through PECVD (Plasma Enhanced Chemical Vapor Deposition). Our main objective is to elucidate the microscopic mechanisms as well as the interplay between atomic level and macroscopic design parameters associated with the development of nano- or micro-scale crystalline regions in the grown film. The ultimate goal is to use multi-scale modeling as a design tool for tackling the issue of local crystallization and its dependence on operating variables. At the heart of our simulation approach is a very efficient, large-scale kinetic Monte Carlo (kMC) algorithm which allows generating samples of representative Si films based on a validated chemistry model. In a second step, the generated film is subjected to an atomistic simulation study which restores the molecular details lost or ignored in the kMC model. The atomistic simulations are computationally very demanding; they are, however, an important ingredient of our work: we use it to back-map the coarse grained model employed in the kMC simulations to an all-atom model which is further relaxed through detailed NPT molecular dynamics (MD) or Monte Carlo simulations. This tunes local structure thus also important morphological details associated with the presence of crystalline and amorphous regions (and the intervening interfacial domains) in the grown film.

The kMC algorithm is based on a carefully chosen set of reacting or active radicals (species) in the gas phase impinging the film and a detailed set of surface reactions. Inputs for species fluxes are taken from a well-tuned plasma fluid model that includes a detailed gas phase chemistry reaction scheme [1,2]. The growth mechanism consists of various surface kinetic events including radical-surface and adsorbed radical-radical interactions, radical-surface diffusion, and surface dissociation reactions. The very fast surface diffusion is decoupled from the rest of the kMC events and is treated deterministically in our work. For a three-dimensional Si(001)-(2x1):H crystalline lattice, our kMC algorithm allows us to simulate film growth over several seconds, resulting in thickness on the order of tens of nanometers. In the following pages we provide more details about the implementation of our kMC algorithm along with validation results.

The n-fold kinetic Monte Carlo method

For the temporal evolution of the reactive surface species, we have used the classic n-fold MC scheme,[3] over a diamond lattice structure. The substrate surface corresponds to a Si(001)-(2×1):H surface and contains 16384 (128x128) Si atoms. The simulation cell has dimensions 22.6nm×23nm and periodic boundary conditions are applied along the (xy) plane perpendicular to film growth. In order to generate a list of all possible events at each time step we developed a kMC propagator, which keeps track of the coordination of all surface Si atoms up to the next-nearest neighbor for each site. The identification of all possible events on all surface sites is carried out through

a parallel implementation that does not demand the exchange of any piece of information between the surface sites.

Decoupled diffusion

In out computational experiments of Si film growth under specific conditions (dilution ratios in SiH_4 varying from 1 to 6%), the surface diffusion reactions are extremely faster than any other reaction in the system. For example, for a brute force kMC simulation the vast majority of computational time (≈99.996%) is spent on tracking the very fast surface diffusive motion of the adsorbed radicals. Therefore we decided to decouple the diffusion reactions from the rest of the kMC events by approximating it as a a Markovian random walk, i.e. by considering the trajectory of the absorbed radicals on the xy plane as a sequence of successive random steps.

Flow chart of the kMC algorithm

1. Initialize computations at time t=0
2. Determine the list of all possible events and select one of them
3. Update system topology and propagate time
4. Identify what type of radicals are adsorbed
5. Choose randomly an absorbed radical and identify its type i^{type}.
6. Choose randomly a new position from its first-neighboring available
7. Propagate time $t=t+dt^{itype}$
8. Repeat steps 5, 6 and 7 n^{type} times for each type of adsorbed radicals
9. Go to step 2
10. Propagate system until a specific film thickness is obtained

Surface Diffusion Verification

Parameters dt^{itype} and n^{type} are system specific and of significant importance, since they control the diffusive motion of the adsorbed radicals. To ensure that the proposed method samples correctly the diffusive motion tracked deterministically, the random walk time step dt^{itype} is adjusted so that the resulting mean square displacement (msd) is identical to that obtained through a brute force application of the kMC algorithm (that is with diffusion being treated as the rest of the reaction events). For all types of diffusive radicals, the self-diffusivity D_s^{itype} is computed from the computed msd via the Einstein equation as:

$$D_s = \frac{1}{4} \lim_{t \to \infty} \frac{\partial \left\langle r(t)^2 \right\rangle}{\partial t} \tag{1}$$

where $<r(t)^2>$ is given by the following formula :

$$\left\langle r(t)^2 \right\rangle = \frac{\sum_{i=1}^{N} \left(r_i(t+\tau) - r_i(\tau) \right)^2}{N} \tag{2}$$

and $r(t)$ is the unwrapped (true) particle position of site i at time t. For a two-dimensional lattice one, can approximate the self-diffusivity via the following equation:

$$D_s = \frac{1}{4} \frac{L^2}{dt} \tag{3},$$

where L is the distance between two neighbouring sites and dt the time needed for a jump between two neighbouring sites. Combining equations 1 and 3 results in:

$$dt = \frac{L^2}{\lim\limits_{t\to\infty} \frac{\partial \langle r(t)^2 \rangle}{\partial t}} \quad (4),$$

from which we determine the value of dt^{itype}. Using this time step in the kMC algorithm ensures a self-consistent treatment of the diffusive motion in the simulations.
The time that adsorbed radicals are allowed to diffuse with a predefined diffusivity between two successive kMC steps is governed by n^{type}. This quantity is of great importance because it determines the diffusion time for each radical and hence the structural properties of the resulting films. The identification of the appropriate value of n^{type} is accomplished by requiring the concentration profiles of the most important structural quantities (dangling bonds and hydrogen content of the corresponding brute force kMC simulations) to be correctly computed in the course of the hybrid simulations. As we can see in Figures 1, 2 and 3 the concentration profiles of all quantities obtained by both methods are in very good agreement. In typical PECVD simulations, the system size increases rapidly with time so that calculations become quickly too slow. Our massively parallel kMC code performs extremely well (see in Figure 4) even when the system size has been increased by more than 30 times.

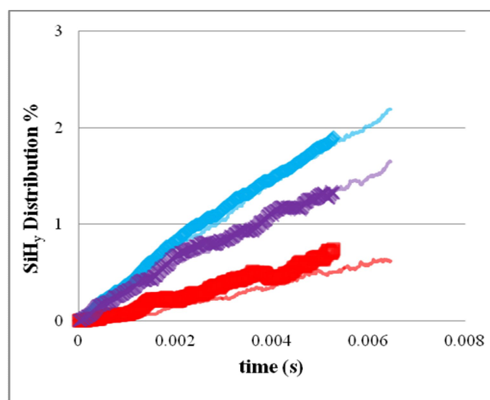

Fig. 1. Time evolution of surface coverage of hydride species. The open symbols correspond to brute force kMC simulation while the noisy lines to the proposed methodology. Red, blue, and purple colors correspond to y=0, 1, and 3, respectively.

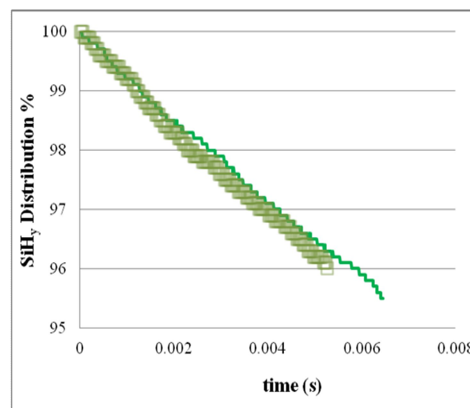

Fig. 2. Time evolution of surface coverage of hydride species. The open symbols correspond to brute force kMC simulation while the noisy lines to the proposed methodology for y=2.

The method has been validated by carrying out several computational experiments over a wide range of dilution ratios and by comparing the numerical results for the growth rate, hydrogen bonding and roughness with data from experimental measurements such as ellipsometry, Raman Spectroscopy, FTIR Spectroscopy and Atomic Force Microscopy, where good agreement has been observed in most cases which should be attributed to the accuracy of the rather detailed and rich (it involves 5 species and 29 reactions) phenomenological chemical (kinetic) model adopted. All kMC simulations have been conducted under industrially

relevant conditions of thin film Si deposition (Pressure=4 mbar. Power = 500 W, Total Flow rate =1 slm, Silane fraction=1 - 6 %).

Currently, the 3-d structures generated with kMC are used as input into large-scale all-atom MD simulations for times up to several nanoseconds to allow the system further relax towards the preferred morphological state at the conditions of the computational experiment. This will allow us to obtain predictions for other industrially relevant quantities and observables (such as the hydrogen content which is experimentally accessible by FTIR and Raman spectroscopy), thus opening the way to fully understanding the conditions and the underlying complex molecular mechanisms responsible for the growth of micro- or nanocrystalline films.

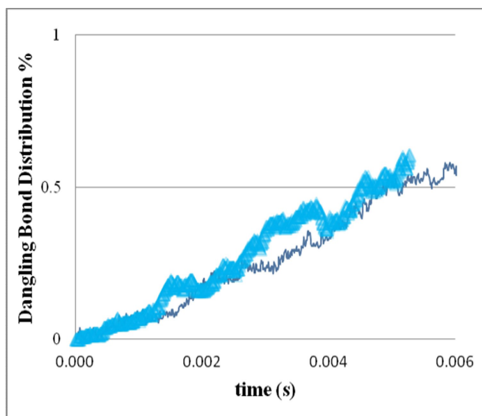

Fig. 3. Evolution of surface coverage of dangling bonds. Open symbols correspond to the brute force kMC simulation while the noisy lines to the kMC methodology.

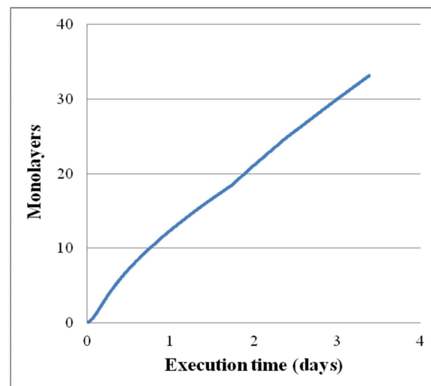

Fig. 4. Evolution of system size with execution time at T=180°C (dilution ratio=3% SiH_4).

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