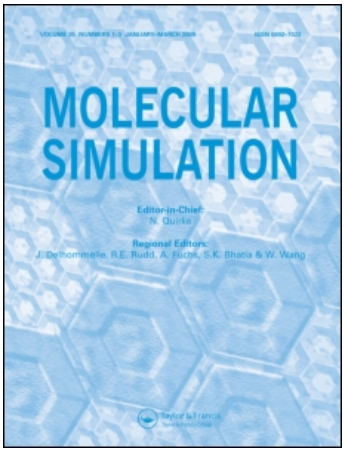

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Kinetic Monte Carlo Predictions of the Conditions Necessary to Grow Helical (Chiral) and Vertical Columnar Structures

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KINETIC MONTE CARLO PREDICTIONS OF THE CONDITIONS NECESSARY TO GROW HELICAL (CHIRAL) AND VERTICAL COLUMNAR STRUCTURES

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Rare Event Dynamics Monte Carlo simulations have been used to investigate the possibility of growing porous crystalline material possessing vertical columnar morphology. This is achieved using a deposition process in which the incoming beam of atoms is held at a grazing angle and, importantly, is rotated azimuthally. For incident beams 80° from normal incidence, rotational speeds of around 1 revolution per second to 1 per 10 seconds were found to produce columnar thin film growth with essentially vertical walls. Slower rotational speeds, around 1 revolution per 30 seconds, produced a helical, but still vertical, columnar structure. Such so-called chiral structures are postulated to be potentially important optical materials. The effect of raising the temperature of the substrate is to decrease the density of the columns, but to broaden their size. This suggests that a temperature-rotational speed set of parameters could be found to produce designer pore sizes with relatively little variation in inter-column spacing and height and either with or without helical structure. Data for one such representation are presented. A movie of the evolution of the nanostructural features of a vertical columnar material is included.

1. INTRODUCTION

It is well known that the morphology of deposited thin films is dependent on the angle of incidence of the incoming beam of particles. For normal, or near-normal, angles of incidence, a smooth crystalline film is usually produced. If, however, the angle of incidence of the beam becomes more glancing, say more than 60° from normal incidence, then the grown material becomes highly porous. The thin films typically show a dendritic-like growth of fingers of material, oriented into the direction of the beam. This effect of

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incidence beam angle can be seen both from simulation and experiment. Experimentally, such porous angled growth has been seen for many materials, from metals to semiconductors. Simulation results from a variety of approaches and sophistication of modeling (Molecular Dynamics, Ballistic Deposition, or Kinetic Monte Carlo Solid-on-Solid models) have also exhibited very similar looking materials. This illustrates that the phenomenon of "non-local shadowing" is a prolific and dominant motif in nature/physics that is only weakly dependent on the nature of the interatomic forces.

While the porous material derived from such studies is interesting scientifically, and has some applications such as solar cells, there is clearly a more practical interest in producing materials in which the columns are vertically oriented (perpendicular to the substrate) and thus do not lie at an acute angle to the surface. An example of this might be an interest in zeolites or carbon storage media in which a constant pore size was desired. One possible way to produce such structures might be to rotate the substrate during deposition and hence have the effect of precessing the beam at a constant incident angle and a continuously varying azimuthal angle. There have been no simulations to test this idea, which provided the motivation for the work described in this paper.

Subsequent to our investigation of the ability to produce vertical columnar growth, we found that similar ideas had been speculated recently in the literature, both theoretically and experimentally [1, 2]. In these studies, the interest was in producing so-called chiral films by deposition at a constant rotational speed azimuthally. The chirality of these films refers to the "handedness" of the optical properties possessed by these helical (and vertical) columns of porous material. Hence, we extended our investigation of vertical columnar material to determine if, and how, we could produce helical but vertical thin films.

In this paper, we describe the use of a Kinetic Monte Carlo (KMC) technique to simulate thin film growth at the conditions necessary to produce vertical columnar and helical (chiral) structures. This involved a study of the effect of rotational azimuthal speed. The choice of KMC for this study is given in the following section. A three-dimensional simulation of the growth of silicon was used as a test case. The effect of substrate temperature on the morphology of the grown films is always an important variable. Here we have investigated its effect for all the classes of material obtained by rotating the sample. In effect we planned to produce a "phase diagram" of the combined effects of substrate temperature and rotational speed.

2. METHODS

A variant of the traditional Kinetic Monte Carlo (KMC) method known as Rare Event Dynamics (RED) [3] was used to simulate the thin film growth in this work. It lacks the accuracy and direct mechanistic information offered by Molecular Dynamics simulations, but it has important advantages in terms of being much less constrained by system size and time scale limitations that adversely affect both the accessible deposition rates and timescales that can be investigated with MD. RED MC efficiently handles large systems (involving up to millions of particles) allowing us to overlap experimental length and time scales for the first time. Systems of 0.5–0.75 million atoms with deposition times of seconds at realistic deposition rates are now possible and are presented here.

As is inherent in RED MC, the silicon atoms are constrained to remain upon discrete lattice sites, effectively giving an Ising model of the silicon lattice. Atomic movement from site to site (one type of event) is governed by a set of predetermined rules. A list is constructed of all the possible events that can occur in the system (or, at least, all the events for which rates can be found !), and then one of these events is selected at random. The probability of choosing a particular event is proportional to its rate, as described below. All events chosen in this way are automatically accepted. The simulation time associated with the selected event is given by the average time before any given event occurs, which is simply the reciprocal of the sum of all of the rates in the system. Since events are automatically accepted, the method is very efficient, even at low temperatures where migration rates are very slow. After the system has undergone this event, the list is updated and the process repeats itself. Simulation continues until the surface has grown to a predetermined level. In this study, we typically grew substrates 200 monolayers high.

The rate at which atoms migrate from lattice site to lattice site is given by an Arrhenius expression incorporating a pre-calculated energy barrier. The energy barriers used here take into account only the local environment (nearest and next-nearest neighbors) of the migrating atom, and are based on experimental results from the Si(100) and Si(111) surfaces [4] and extrapolated to other configurations. Atoms are allowed to jump to any vacant nearest neighbor site as long as its destination has at least one other nearest neighbor. This prevents atoms from diffusing off the substrate. In addition, atoms are permitted to jump to vacant second nearest neighbor sites. Without these moves, a single adatom would not be able to diffuse on the (100) silicon surface on which neighboring surface sites are second nearest neighbors.

The deposition of an atom onto the surface is included as simply another event in the simulation. Starting from a nondiscrete random location above the growing surface, an incident atom is brought to the surface at the desired angle of incidence and azimuthal angle. The point at which the incoming atom first collides with a substrate atom is determined by incrementally moving the incident atom along its trajectory and searching the local area for the first possible interaction. An impact parameter is then determined for the collision, and an energy transfer associated with the collision is calculated. If the energy transferred to the surface atom is greater than a set threshold, then the incident atom sticks to the surface at the nearest vacant lattice site. Otherwise the atom is considered to have glanced off the substrate atom, and leaves the system.

Periodic boundary conditions are employed in the plane of the substrate. Initially the cells contain 4 substrate layers, with an exposed and bulk terminated Si(100) surface orientation. A fixed substrate was placed beneath this initial layer, which acted as a sink for any vacancies that might diffuse into it and provided neighbors for atoms in the lowest levels of the initial substrate.

The method outlined here provides the opportunity to simulate a wide range of conditions. Typical system sizes explored here ranged from 400,000–800,000 particles. The cell sizes are 200 monolayers in each of the three Cartesian directions. This represents samples of roughly 27 nm per side. The substrate temperatures studied here ranged from 200–700 K. Typical experimental studies range from room temperature (300 K), for metals, to about 900 K. The temperatures accessible to RED MC are limited to below around 900 K for this system. Above these temperatures the RED technique loses efficiency as moves with low energy barriers dominate the simulation and the time-step becomes exceedingly small. For the system sizes studied here, simulations performed above temperatures of approximately 650 K do not cover sufficient time to allow the morphological features of the thin film to develop before the substrate reaches the top of the cell and the simulation terminates. The size of the cell is limited by the amount of memory available, as described below.

The RED method requires maintaining large lists of events and manipulating them in an efficient manner. A binary tree structure containing all of the events allows for a very efficient selection of events and also for propagating rate data for the time step calculation. However, these large lists can consume prohibitive amounts of memory (approximately 2 GB for the work presented here). Thus available memory is typically the limiting factor of the maximum possible simulation size. This may manifest itself as

an upper limit in temperature that can be studied, as described in the praragraph above.

3. RESULTS AND DISCUSSION

The RED MC method described above was used to perform a set of identical simulations observing the growth of Si thin films on a Si (100) surface differing only in the rate of rotation of the incident beam and the substrate temperature. Note that in the simulation (unlike analogous experiments) it is easier for us to rotate the incident beam of atoms than to rotate the substrate. This, of course, has no effect on the results. In all these simulations, the incident angle of the beam was held at 80° from normal incidence, a grazing angle known to produce highly porous columnar structures for a wide range of conditions (of substrate temperature and deposition rate). Any incident angles above approximately 60° would have been a possible choices of beam incidence since these also produce columnar growth, however the effect is more pronounced at high angles such as 80°, especially at higher substrate temperatures where diffusion can partially overcome the effects of non-local shadowing.

The effect of changing the deposition rate of atoms to the surface was not closely examined since we have found that deposition rate and substrate temperature exhibit similar, but inverse, effects. That is, increasing the temperature is akin to lowering the deposition rate to a first approximation. This seems intuitively reasonable for moderate to high temperatures (above 500 K). We feel that the important parameter is actually the ratio of deposition events to diffusion events. Varying either deposition rate or temperature can affect this ratio.

RED MC simulations were performed for temperatures from 100–650 K (the whole accessible range of RED MC for this system) and for deposition rates from 1 revolution of the sample per second to 1 revolution per 30 seconds. Slower rotational rates are, of course, possible. At some limiting speed, the growth morphologies are likely to appear to revert to the slanted columnar structures characteristic of non-local shadowing *when viewed on the size scale of our simulation.* However, we believe that the effect of rotation will be persistent but manifested on increasingly larger lengthscales as the rotational speed decreases.

The simulations performed here produced a matrix of structures, all of which produce vertical columnar structures. An example of the evolution of such a vertical columnar structure is shown in the movie listed as "Figure"1.

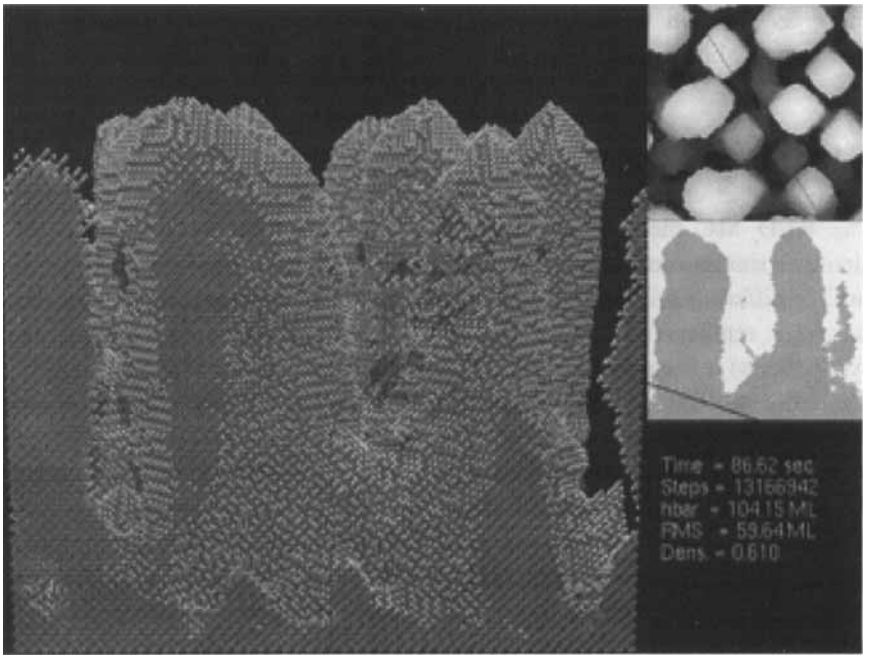

FIGURE 1 Animation of the evolution of growth of the vertical columnar film. Each frame is divided into four sections. The large section on the left shows a 3-D perspective of the growing surface. Bulk-like atoms with 4 nearest neighbors are shown in green; atoms with other coordination numbers are shown in tan.

The direction from which the incident beam is originating is depicted by a red and white arrow.

The upper right section of the frame is an AFM-like representation of the surface where brighter corresponds to higher. A projection of the incident angle is given by a red line.

The middle right section is a cross-sectional view horizontally through the center of the substrate. Again a projection of the deposition angle is shown in red.

The bottom right section shows various numerical data including the elapsed time, the number of KMC events, the average substrate height (in monolayers), RMS roughness (in monolayers), and the substrate density expressed as a fraction of the occupied lattice sites.

Since without substrate rotation the columns grow only in the direction of incident beam, although usually with a slightly reduced angle [5, 6], the vertical structures produced above are the result of the azimuthal rotation. When the substrate (or beam, in this case) is rotated, the columns are continually changing their direction of growth into the beam. If the substrate is spun at a high enough rate, the columns never have the opportunity to grow in any single lateral direction to any extent. However, no matter what the azimuthal angle of incidence, there is always a vertical component of the growth. The result is a vertical column, normal to the substrate.

The tops of the growing tips, akin to meristems in biological systems, are not flattened or rough on an atomic scale. Instead, the diffusional processes by which atoms seek low energy sites, produce faceted pyramidal tops to the meristems, where the facets generally exhibit low energy (111) orientations. This can be seen in Figure 1 and the cross-sectionl views of Figure 2.

If the substrate is spun at a slower rate, the columns have a limited opportunity to grow significant amounts in a lateral direction. Again, the substrate always grow "up" since there is always a vertical component to the growth direction. In this case, the growth front (meristem) develops in a circular path following the location of the oncoming beam. The result is a helical-like structure, which could be described as chiral, in the parlance of recent papers in this area. This effect can be seen most clearly in Figure 2 in the cross-sectional views. At low rotation rates (rotational period = 30 seconds, say), a clear zigzagging of the columns is seen, which when expanded three-dimensionally corresponds to a helical structure. Characterization of the helicity of the columns is difficult, and somewhat subjective at this point. However, two clear trends exist in the results. First, if the sample is rotated at a high enough rate, straight vertical columns can be grown. Second, decreasing the substrate temperature requires a corresponding increase in rotational rate in order to continue growing straight vertical columns.

The effect of substrate temperature is quite pronounced and can be seen in Figure 2. At low temperature (below 400 K), the amount of diffusion is very small since the diffusing atom do not have enough energy to surmount their migration energy barriers. The result is akin to ballistic deposition simulations, in which there is no diffusion. A very porous, flake-like and heavily defective film is produced. As the substrate temperature increases and diffusion begins to occur, the atoms are able to find favourable sites with many neighbors. The result are localized areas of essentially defect-free film (the columns) separated by large voids between them. As temperature increases further, diffusion events dominate the simulation, and are able to partially overcome the effects of non-local shadowing, at least within the confines of our simulation. The result, as seen in the rightmost column of Figure 2, is that the columns did not have an opportunity to develop in the timeframe of the simulation.

With increased diffusion, atoms are able to diffuse about the surface more readily. Once the atoms are deposited, they are more easily able to find low energy sites (such as (111) surface sites). The effect is increased lateral diffusion resulting in a broadening of the column.

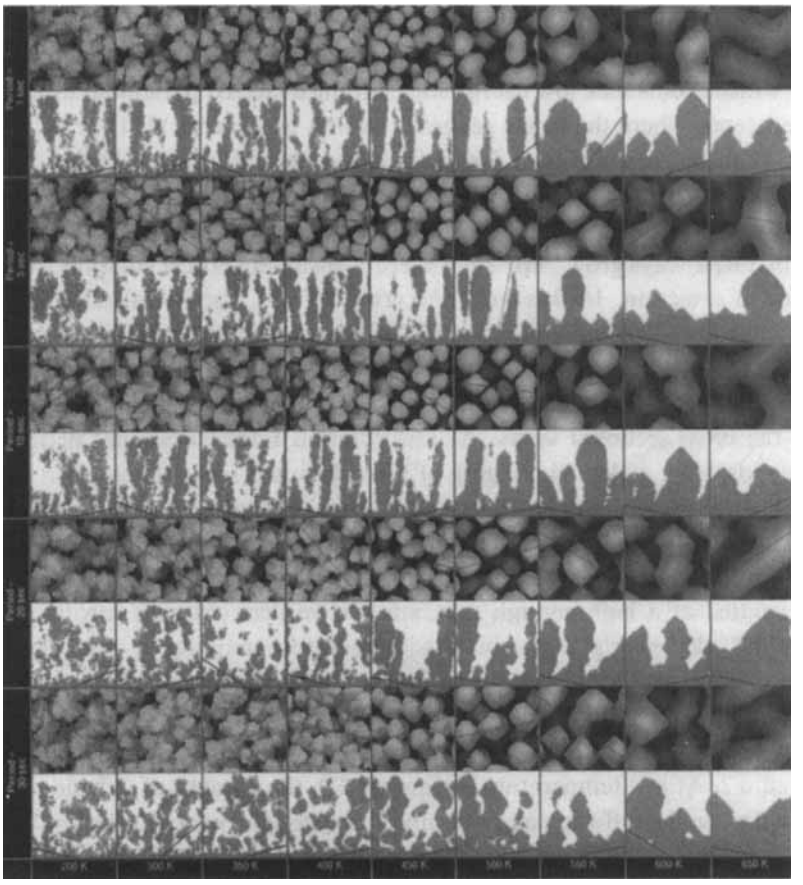

FIGURE 2 Effects of substrate temperature and rate of sample rotation. Each location in the grid represents a view of a completed simulation run at the conditions indicated on the axes. Each view is comprised of an upper and lower section. The upper section is an AFM-like representation of the surface where brighter corresponds to higher. The lower section is a cross-sectional view horizontally through the center of the substrate. In both frames, residual lines can be seen which represent the projection of the incident beam at the completion of the run.

Substrate density was also briefly examined. Although varying the rate of rotation can change the local structure of the columns, the overall substrate density remains unaffected. At low temperatures in which there is no diffusion (below 400 K), the defective flaky structure produces a very low density substrate (about 25% of the available lattice sites are occupied). If the simulation did not constrain atoms to remain on lattice sites, it is likely that an amorphous structure would have resulted instead. Once above the temperature where diffusion sets in, there is no significant change in the

density of the porous portions of the grown films (approximately 40% of the available sites are occupied). Although the columns are broader as temperature increases, the voids are wider as well. The same amount of deposited material is simply distributed in a different way.

4. CONCLUSIONS

Rare Event Dynamics Monte Carlo simulations predict that vertical columnar thin film morphologies grown on a diamond cubic lattice, like Si, can be produced if the substrate is rotated continuously in an azimuthal direction, while holding the incident beam at a glancing angle above 65°. Given the known pervasiveness of non-local shadowing phenomena, we suggest that this kind of growth is unlikely to be limited to silicon-like materials. Rotation periods above about 20 seconds give rise to vertical walled pores with fairly regular inter-pore separation and height. This suggests that novel materials could relatively easily be produced with morphological structures appropriate to applications for which a uniform pore size is important. As substrate temperature increases, above about 500 K, the pores are essentially defect-free.

If the rotational speed of the substrate has a period of 20 seconds or more, helical but still vertical thin film structures are produced. We suggest that rotating the substrate below this threshold will always produce helical films, although this is unlikely to be visible in the microscopic "window" afforded by simulations. RED MC simulations at very slow rotational speeds will show one part of the helix and it may appear as if the non-local shadowing has returned. Further work is needed to characterize the helical nature of these intruiging virtual materials.

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