Study of Silicon Thin Film Growth at High Deposition Rates Using Parallel Replica Molecular Dynamics Simulations

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Abstract

Atomic processes and structural configurations during thin film growth of silicon are studied by performing parallel replica molecular dynamics simulations. These simulations reveal that complex many-atom moves can occur at large deposition rates during silicon thin-film growth, which can affect the long-time evolution of the film. The types of atomic moves change as thickness of film varies from 0-2.3 ML. Single-atom moves are common at low Si coverage. However, surprisingly fast many-atom moves are observed at higher film thicknesses when amorphous thin-films are formed. Implications from this study on the observations that can be made with standard materials modelling approach such as molecular dynamics and kinetic Monte Carlo simulations are discussed.

Keywords: Thin-film growth; silicon; accelerated molecular dynamics; parallel computation; many-atom moves

Nomenclature

PRMD parallel replica molecular dynamics
TPMD temperature programmed molecular dynamics
KMC kinetic Monte Carlo
MD molecular dynamics
ML monolayer

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Selection and peer-review under responsibility of Organizing Committee of ICAER 2013

doi:10.1016/j.egypro.2014.07.270
1. Introduction

Thin film growth is an important step during fabrication of photovoltaic devices. Typically, deposition techniques such as ion-beam deposition, Chemical Vapor Deposition, Physical Vapor Deposition, Atomic Layer Deposition, sputtering and Molecular Beam Epitaxy are used to grow thin films on a substrate material by depositing the material atom-by-atom [1, 2]. The deposition conditions namely, the deposition rate, temperature, pressure and deposited species are known to strongly influence the structure morphology [3, 4], degree of crystallinity or amorphous structure [5], composition profiles (in the case of multicomponent thin-films) [6], surface reconstruction [7], film roughness [8-10], grain-size distribution [11, 12], types and concentration of defects, and the electronic, chemical, mechanical and optical properties of the thin films. In recent years, improvements in our understanding of the physics and chemistry of films, surfaces, and interfaces have aided the fabrication of compound photovoltaic devices [12, 13]. However, our ability to control the film structure and properties depends largely on the availability of predictive models for thin-film growth [14-16]. For instance, fundamental understanding of materials defect formation and evolution could enable strain-engineering and reduce the defect concentration in the film [17, 18].

In this work, we study thin-film growth of silicon. Silicon is an important material in the multibillion dollar semiconductor industry with applications ranging from optical devices, LEDs, integrated circuits and photovoltaic cells [19]. Moreover, the study of homoepitaxial films is easier due to absence of elastic interactions originating from lattice-mismatch present in heteroepitaxial films. The growth of Si thin films is inherently multiscale in nature (see Fig. 1). It is known that Si(001) reconstructs to form dimer row structures. Growth of a thin film is governed by adsorption, diffusion processes, nucleation and coalescence processes as shown in Fig. 2. The rate constants associated with these atomic moves can vary by orders of magnitude. Any predictive dynamical model for film-growth should incorporate all the relevant atomic mechanisms present in the system [20-22]. As thin films are deposited material defects such as vacancies, interstitials, dislocations and/or grain boundaries can be introduced into the crystal structure [23-33], which affect the semiconductor opto-electronic properties. The dynamical model should be capable of describing the defect formation and migration. In addition, the film roughness, film composition and interfacial structure also evolve at various length and time scales [10, 34-37]. Consequently, a multiscale model for thin film growth that can span atomic length and timescales (Å and ps, respectively) to device length and timescale (several mm and min, respectively) is needed. As we describe next, this is a challenging problem.

Standard techniques to study the evolution of thin films are continuum method, kinetic Monte Carlo method and molecular dynamics. Continuum methods based on deterministic or stochastic partial differential equations are formulated using basic principles of conservation of energy, mass, momentum. Although these models can reach large timescales, they are phenomenological and cannot describe microscopic physics accurately [38-41]. KMC method is a powerful simulation technique [42-44]. However, it is computationally more expensive than continuum models. Although, the correct microscopic physics can be introduced in KMC, the main challenge is that the input to KMC (in terms of atomic processes and their associated rate constants) can be obtained only by using more computationally expensive molecular simulation techniques[21, 22]. As we shall describe later, we observed many atomic processes in our simulations that are typically absent from KMC models used for studying thin-film growth. One can thus conclude that the predicted film growth obtained from standard models could be incorrect. MD method[45] can provide the exact dynamics using interatomic potentials. One can find atomic processes such as bond-formation and breakage events and diffusion processes using MD. However, MD can only reach up to nanosecond seconds with current computational resources. On the other hand, deposition of hundreds of monolayers and macroscopic timescales are possible when a KMC model is available. Hybrid KMC-MD methods developed recently take advantage of both methods, however, there is no control over the accuracy of the method. Another possible way of enabling access to larger timescales with MD is by using accelerated MD techniques [46], such as hyperdynamics, parallel replica dynamics and temperature accelerated dynamics. In this work, we have simulated the deposition of Si atoms on a Si(001) surface using Voter’s Parallel Replica Molecular Dynamics method . The goal of this work is to employ PRMD to i) study the types of material structures and atomic processes that are observed with high deposition rates, ii) study the speed-up of PRMD over the MD method, and iii) understand the advantages and disadvantages of the PRMD method in comparison to KMC method.
The outline of this paper is as follows. In Sec.2, a brief description of the PRMD method and our simulation procedure is given. In Sec. 3 & Sec. 4, we discuss the results obtained with the PRMD simulation of Si thin-film growth and its implications. Finally, conclusions are presented in Sec. 5.

![Diagram](image)

**Fig. 1.** Important dynamical processes spanning atomistic to device length and timescales during thin-film growth of Si for photovoltaic applications. One of the main challenges involved in developing predictive models for thin-film growth is the requirement to accurately describe each of these processes.

![Diagram](image)

**Fig. 2.** Atomic processes present during growth of silicon thin-film. Filled circle denotes an atom, while empty circle denotes a vacancy. Our model developed includes all the atomic processes shown except for desorption.

## 2. Simulation Procedure

Our simulation method consists of two main steps: i) Si deposition and ii) diffusion events. The deposition of Si atoms is performed using standard MD method. The deposition rate is fixed to $10^8$ atoms/sec. There are 25 deposition stages. In each stage, 12 atoms are randomly deposited on the (001) surface. This rate is orders of magnitude larger than the typical experimental deposition rates. The purpose of these calculations was to identify the types of material structures with high deposition rates and to make comparisons to experimental observations. We performed 10 diffusion moves after each deposition stage using PRMD. These steps were performed till a film thickness of 2.3 ML was reached.

Timescales of nanoseconds are accessible with conventional MD, whereas PRMD can reach longer timescales. The time reached is proportional to number of parallel processors used [48]. In PRMD, the state-to-state evolution of the system in the potential energy surface is followed using M parallel processors (see Fig. 3). PRMD assumes that the atomic moves occur at timescales much larger than the vibrational timescales and that the times at which they occur obey the exponential probability density function $p(t)=k \exp(-kt)$, where $k$ is the rate constant for the
atomic move. A replica of a state is provided to each parallel processor. Each processor then performs MD and searches for an escape from the state of the system. Escapes are found by performing an energy minimization calculation with the current atomic positions and finding whether the system has moved to a new basin (see Fig. 3). Note that the escape corresponds to an atomic move. After a successful escape from a replica is observed, the MD calculations being performed by all other processors are stopped. The system moves to a new state based on the observed escape. The time is incremented by total MD time spent by all processors while searching for an escape from the state. Since the escape time still obeys the probability density $p(t)$, the time accrued by each processor is much smaller than the actual escape time. The PRMD method reduces to standard MD in the case where $m=1$. However, an overhead due to cost involved in searching for escapes makes the PRMD calculation slightly more expensive than MD for $m=1$. In our PRMD calculation, a CPU time of 2 days was reached using 50 parallel processors. More discussion on the speed-up from PRMD is provided later. The Stillinger-Weber interatomic potential [49] for Si, which can accurately describe many aspects of bulk and surface Si, was used with our MD and PRMD calculations.

![Fig. 3. Schematic showing the working of parallel replica molecular dynamics (PRMD) method from a state in the potential energy basin using M parallel processors (following Ref. [47]). State of the system is denoted by circle. More details are given in text.](image)

3. Results

A Si slab consisting of 3072 atoms with a crystalline diamond cubic structure was prepared. The surface atoms of Si(001) spontaneously reconstruct to form dimer rows using MD (see Fig. 4). This surface reconstruction behavior is in agreement with experimental observations. The average bond length of dimer row atoms obtained in the MD simulation is 2.4 Å, which is close to experimental value of 2.35 Å. The reconstructed rows were created within 10$^{-12}$ s, which is insufficient for the system to form perfect dimer rows and leads to defects in the surface. As shown in Fig. 4, we observe two types of defects, namely, broken chain dimer rows and buckled dimer atoms. Defects in the reconstructed rows reported in literature include one dimer pair missing, two dimer pairs missing, two adjacent silicon atoms missing from the dimer row, buckled dimers and split dimers [50, 51]. Although, we observed two types of defects, we did not observe the other defects in the reconstructed surface. This could be because of the fact that less time given for the reconstructed surface to reach equilibrium and the small system size chosen for our simulation. As discussed later, we found in our simulations that surface defects do not affect the type of film deposited on surface at high deposition rates.
During the first deposition stage, 12 atoms were randomly deposited on the surface (Fig. 4). Atoms can form dimers and trimers in this first stage. Past studies have shown that the deposited atoms reside on dimer rows for Si(001) surface at low coverages. We observed similar behavior in our case. There are different types of adatom moves on the surface. In our calculations, an isolated adatom on the Si(001) surface undergoes back-and-forth motion on the dimer as shown in Fig. 4 (processes A and B). The adatom covers a distance of 3.55 Å in a single move. Atomic moves such A and B are very fast and are frequently observed at timescales of $10^{-11}$ to $10^{-9}$ seconds.

Past studies have mentioned that a hop move along the dimer row can also occur, which is more preferred (activation barrier of 0.6 eV) than an adatom hop across two adjacent dimer rows (activation barrier of 1.0 eV) [52-54]. However, these moves were not observed with our PR MD calculations. We conclude that the rate constant for the back-and-forth motion of atom on the dimer row must be larger than the rate constants for the other types of moves, which explains why the back-and-forth motion is frequently observed at low coverages. We also found that a single atom on the dimer row can split the dimer atom pair. We investigated the fast adatom moves separately by preparing a perfect reconstructed Si(001) surface with a single adsorbed Si atom. 100 escapes from the starting state were observed. It was found that the probability density of the fast escapes was given by the exponential distribution $p(t)=k \exp(-kt)$. The maximum likelihood estimate of the rate constant $k$ was obtained as $3.7 \times 10^{10}$ s$^{-1}$, i.e., the average time for the move is $2.7 \times 10^{-11}$ s. The value of the rate constant explains the timescale of the moves observed with PRMD.

After one monolayer is deposited, the original surface dimer atoms rearrange to form diamond cubic structure while monolayer surface forms either dangling bonds or a dimer pair (Fig. 5a and b). For example, the adatoms colored blue, which were deposited in the first stage, are bonded to three or fewer atoms, while the adatom colored red, which was deposited during the second stage, is bonded to three atoms. The local bonding of initial dimer row atoms changes from tetrahedral structure to crystalline structure in subsurface. We observe that the deposited atoms tend to form either a dimer with an adatom existing on the surface or a cluster or an island at different stages of deposition. This shows that a rich variety of structures are possible as atoms are deposited on the surface. As the deposition proceeds, the atoms that have just been deposited form dimers with the previously deposited atoms. Based on our past experience with metals and semiconductor materials, we expect that as the local environment of the atoms changes, the types of processes and their rate constant will also change [55-57]. We indeed observe more complex moves at later stages of deposition.
Fig. 5. Deposited atoms have dangling bonds after the (a) first and; (b) second stages of deposition. Similar situations occur at later stages.

Fig. 6. (a) Initial and; (b) final positions of adatoms (labeled A, B and C) involved in three different moves after the fifth deposition stage. Panels (c) and; (d) show the initial and final positions of heptamer-atoms involved in a move after eight deposition stage.

Fig. 6a and b depicts the initial and final positions of three adatoms that participate in hop, exchange or buckling moves during the fifth deposition stage. Unlike, single- or two-atom moves, which were observed at the early deposition stages, complex many-atom moves are observed at higher film thicknesses. In Fig. 6c and d, the initial
and final position of heptamer-atoms involved in a many-atom move is shown. Other complicated moves on the surface are shown in Fig. 7a and b. Many of these moves are counter-intuitive, because they occur at pico-seconds timescales and are faster than the rare-events such as exchange moves even though more number of atoms are participating in the move. Assuming that all processes have the same pre-exponential factor, i.e., we expect that the faster processes tend to occur more frequently because of a low energy barrier, while rare events have a high energy barrier. Therefore, it is difficult to observe the rare-events in our PRMD calculations. These observations have important implications in the way standard KMC models are created and employed to study film growth. Standard KMC models consist of a catalog of atomic moves based on our understanding of the atomic processes in the system. Usually, single adatom moves are included in such models. Because the many-atom moves we have found in our study are not well understood or because it is difficult to guess these types of moves such moves are ignored in the standard KMC models. One of the strengths of PRMD is that we can learn about the types of atomic moves in a system without prior knowledge of the moves. This information can be used as an input to a KMC model.

Fig. 7 (a) Initial and; (b) final position of outlined atoms participating in two different moves. The first move involves a hexamer, while the second move involves a tetramer; (c) Surface of the film after last deposition stage.

It is known that at low deposition rates the monolayer formation results in smoother surface with few islands. As more atoms are deposited, the surface becomes rough (see Fig. 7c). The surface roughness is present because the deposited atoms do not have enough time to form a layer due to the high deposition rates. It is observed that after 2.3 ML, 4 layers of atoms are present in some locations while there are positions where atoms have not deposited yet. At higher rates, the island formation leads to increased roughness, as we have observed in our study.

PRMD method has an advantage over MD, namely, that the computational cost is reduced linearly with number of processors used. We found that our PRMD calculation requires an average time of 8 μs/atom/step compared to MD which requires 100 μs/atom/step. Thus a speed-up of 12 times is observed. The total time reached after 2.3 ML were deposited was 0.85 μs. Clearly, the use of PRMD has provided insights into the types of complex moves that need to be included in the KMC model. In our case, we have allowed 10 atomic moves to occur with PRMD after each deposition stage. The number of moves are insufficient to observe rare atomic processes. In order to observe rare events, roughness on the surface, grain size defects and formation of dislocations, we will need to perform simulations reaching much longer timescales. Faster moves compete with rare events, and diminish the possibility of the occurrence of rare events. These observations lead to the conclusion that although PRMD is more efficient than standard MD, it cannot reach physically relevant timescales during thin film growth. Newer computational techniques are required that can reach even longer timescale while maintaining the accuracy of PRMD.

4. Implications

We had mentioned earlier in Sec. 1 about the need for computational tools that can provide insights into processes at the molecular scales, while reaching time scales that are much longer than those accessible to standard
molecular simulation techniques. The results obtained in this work clearly highlight that interesting types of processes occur at nanosecond time scales that can influence the atomic configurations at longer timescales. This study also gives us a better understanding of some of the strengths and weaknesses of the PRMD method.

The advantages of PRMD technique are:
- very few assumptions are involved; the main assumption is that atomic moves are first order processes,
- as accurate as molecular dynamics,
- longer timescale can be accessed by parallelizing any standard MD code,
- implementation of the parallelization step is straightforward unlike the parallelization steps involved in domain-decomposition or hybrid methods,
- can observe atomistic moves with low energy barrier (< 0.2 eV typically),
- phenomena such as deposition, defect formation, diffusion, many-atom moves can be studied simultaneously.

The disadvantage of PRMD technique is:
- atomic moves with large energy barrier, i.e., small rate constant, are difficult to observe with PRMD. In our simulations we reached 0.85 μs time, however, reaching millisecond process was not possible with PRMD.

For overcoming the limitation of the PRMD method, one possibility is to exploit the presence of superbasins in a potential energy surface. In the Si-system studied in this work, the system was trapped in a collection of states that we term a superbasin [58]. The system moves from one superbasin state to another via fast moves, however, an escape out of the superbasin is rare. This results in a separation of timescales between the fast and the rare moves. We have recently developed the temperature programmed molecular dynamics (TPMD) method [59] that can achieve excellent speed-up over standard MD by assuming that the system attains equilibrium when it is present inside the superbasin and allows the system to escape from the superbasin with a large time step. Future studies with TPMD will enable us to study the atomic moves and configurations during thin film growth over longer timescales.

5. Conclusion

We have employed parallel replica molecular dynamics method for studying the growth of silicon thin-film over Si(001) surface at large deposition rates. During the growth of the film from 0 to 2.3 ML, we find that different types of material structures can be found because amorphous films are formed over the crystalline substrate. The material structures include isolate adatoms, dimers, larger clusters and rough film surfaces. Due to changing local environment, different types of atomic processes are also observed. Several atomic moves are counter-intuitive as they include more than 3 atoms, yet their rate constants are very large. Such moves can result in fast rearrangements at the surface. Typically, such atomic moves are absent from standard KMC models. We believe that this shortcoming of standard KMC models can significantly compromise their accuracy. The ability of PRMD to automatically find the atomic processes in the system can be exploited to build better KMC models that contain all relevant atomic moves. We find that the calculation would have taken several days for one monolayer calculation using only molecular dynamics on a single processor. Whereas, our PRMD simulation just took 2 days for completion with a computational speed-up of more than 10 times over MD. Larger speed-up can be obtained with larger number of processors. However, we conclude that the timescales that need to be accessed are several orders of magnitude larger than what is presently accessible with PRMD. Newer computational techniques such as the TPMD method are required that can study the rare event processes that occur at longer timescales.

Acknowledgements

We acknowledge the support provided by Centre for Development of Advance Computing (CDAC), Bangalore, India and IIT Kanpur, India. We also acknowledge help provided by Ms. Shraddha Mule in implementation of the Stillinger-Weber potential for Si.
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