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Solution processed deposition of electron transport layers on perovskite crystal surface—A modeling based study

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ABSTRACT

The power conversion efficiency (PCE) of planar perovskite solar cells (PSCs) has reached up to ~20%. However, structural and chemicals defects that lead to hysteresis in the perovskite based thin film pose challenges. Recent work has shown that thin films of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) deposited on the photo absorption layer, using solution processing techniques, minimize surface pin holes and defects thereby increasing the PCE. We developed and employed a multiscale model based on molecular dynamics (MD) and kinetic Monte Carlo (kMC) to establish a relationship between deposition rate and surface coverage on perovskite surface. The MD simulations of PCBMs dispersed in chlorobenzene, sandwiched between (110) perovskite substrates, indicate that PCBMs are deposited through anchoring of the oxygen atom of carbonyl group to the exposed lead (Pb) atom of (110) perovskite surface. Based on rates of distinct deposition events calculated from MD, kMC simulations were run to determine surface coverage at much larger time and length scales than accessible by MD alone. Based on the model, a generic relationship is established between deposition rate of PCBMs and surface coverage on perovskite crystal. The study also provides detailed insights into the morphology of the deposited film.

1. Introduction

Developing highly efficient solar cells that employ inexpensive nanostructured materials as well as a low-cost production technique is necessary to fulfill the ever increasing energy requirements. Of the wide range of thin-film solar cells currently being explored, perovskite solar cells (PSCs), which are based on inorganic-organic lead halide perovskites, have shown remarkable improvement in power conversion efficiency (PCE) over the last six years [1–3]. The key factors that have enabled such high PCE in PSCs include high optical absorption coefficient, long diffusion length of electrons and holes, long carrier lifetimes, good carrier mobility and tunable optical band gap by varying chemical compositions [2,4–8].

Based on device architecture, perovskite solar cells can be classified into two categories, namely mesoscopic PSCs and planar PSCs [9]. In PSCs with mesoscopic structure, the photo absorption layer consists of a blend of perovskite material and mesoporous scaffolds of nanometer sized metal oxides, such as TiO_2. These photo absorption layers are sandwiched between thin films of electron transport layer (ETL) and hole transport layer (HTL) in the PSCs. Nanometer sized mesopores act as electron harvesting sites, which diminish the requirements of long minority carrier drift and diffusion [10,11]. Due to the presence of local electron harvesting sites, mesoporous PSCs achieve high PCEs of ~20% [12]. However, synthesis of mesoporous scaffolds requires high temperature processing. For instance, mesoporous TiO_2 requires processing temperatures above 450 °C, which is an impediment in large scale production of mesoporous PSCs [13]. To overcome the challenges of high processing temperature, PSCs with planar device architecture, with relatively low processing temperature (<150 °C) requirements, were introduced [13]. As in their mesoporous counterpart, the perovskite material in planar PSCs is sandwiched between compacted HTL and ETL that eventually collect charges [13–15]. Cost effective conventional solution processing techniques, such as spin coating, slot-die coating and role-to-role processing techniques can be employed to fabricate planar PSCs [16,17]. However, planar PSCs have some disadvantages compared to mesoporous PSCs, such as presence of excess halides (antisite defects) on perovskite grain boundaries, trap states and surface pin holes, which cause hysteresis and current instabilities and reduce the PCE of planar PSCs [18–22]. Various strategies have been explored to reduce these structural defects. Recently, Xu et al. [20] reported that a separate thin film of PCBMs on perovskite surface or PCBMs incorporated within the perovskite structure acts as ETL and suppresses the

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Pb-I antisite defects by forming thermodynamically stable bonding between PCBM and Pb-I antisite defects. Therefore, presence of PCBM in either form reduces hysteresis, recombination losses and surface pin holes. As a result, planar PSCs with fullerene/fullerene derivative based ETL have achieved efficiencies of up to 19.1% [21]. In planar PSCs, the thickness of ETL, such as those based on thin films of PCBM, is extremely important. While a thick layer of PCBMs may increase series resistance and thus decrease conductivity, films that are too thin may lead to insufficient coverage of the perovskite surface [23–25]. Insufficient coverage of the surface reduces the interfacial area between perovskite and PCBM based ETL and in turn decreases the number of transferred electrons from perovskite to electrode through the ETL.

The morphology of the solution-processed film, which inherently depends on self-assembly of PCBMs on perovskite surface during solution processing, is therefore extremely important in determining the performance of planar PSCs. The morphology depends on several factors, such as the concentration of the stock solution, choice of solvent, deposition time, evaporation rate and nature of the exposed crystalline perovskite surfaces [26,27]. Molecular interactions between the PCBMs and the perovskite surface determine the nature of self-assembly of PCBMs on the surfaces and propensity to form nuclei for further film growth [28]. In turn, the growth of nuclei to form monolayers on perovskite surfaces determines the final quality and morphology of the thin films [29]. However, achieving stringent control over morphology, optimum thickness of thin films and complete surface coverage with few defects, during solution processing of thin films is a challenging task and requires lots of trial and error based experiments. On the other hand, atomistic modeling tools can account for molecular interactions and provide theoretical insights in to the self-assembled structures of PCBMs on perovskite surfaces at a range of experimental conditions and therefore can be leveraged to determine optimal conditions for film growth.

Molecular dynamics (MD) simulations, in particular, is able to account for van der Waals (VDW) and long range Coulombic interactions between different solute particles [31] and that between solute and substrate and has been employed to model surface deposition during processing of thin films [30]. Our recently published work has demonstrated the efficacy of MD simulations in determining the dominant interactions of the atoms of PCBMs with perovskite surfaces and resulting configuration [32]. Moreover, MD simulations can capture the inherently fast dynamics of changing molecular states, such as deposition events that occur in time scales of picoseconds and can therefore determine the number and nature of nucleation sites for film growth within short time and length scales [30,33]. However, MD is limited to time scales of ~0.1 μs and length scales of ~0.1 μm. On the other hand, in order to inform device-scale fabrication processes, it is necessary to analyze surfaces that have several orders of magnitude larger areas that are exposed to deposition for significantly longer times. Therefore, it is necessary to develop a multiscale model that accounts for atomistic interactions while predicting deposition rates, kinetics of monolayer formation and mechanism of further film growth during solution processing of thin films at the device-level. Kinetic Monte Carlo (kMC), which is based on a stochastic framework and is reliant on rates for changes in molecular states, can dynamically scale up to much larger length and time scales. Therefore, kMC can potentially leverage the capability of MD simulations [34] to access rates of molecular-scale events and determine statistically meaningful deposition characteristics, predict size and shape of nucleation sites on substrates and simulate growth of nucleation sites to complete monolayers during solution processing of thin films.

In this study we report results from an in-house multiscale model, which combines MD simulations and kMC, to study the self-assembly of PCBM on perovskite surface terminated by (110) plane. We have used MD simulations to explicitly account for molecular interactions between PCBMs and perovskite surfaces, define unique deposition events and determine their rates. The rates from MD simulations were applied as inputs to the kMC module to scale up to time scales of ~1 μs and length scales of ~0.1 μm. Based on our model, we calculated the deposition rates, surface coverage and size and shape distribution of PCBM nuclei on perovskite surfaces. Our model was able to correlate the morphology and quality of thin films with the concentration of stock solution during solution processing of thin films. The insights gained from this study will help to predict optimum process parameters to achieve improved surface coverage of the deposited ETL while maintaining low defect concentrations.

2. Methodology

In order to study the growth rate and morphology of PCBM monolayers deposited on perovskite surfaces, at length scales relevant to planar PSCs, we developed a model that employs a combination of MD and kMC methods. Typically, the growth of a monolayer due to the deposition of PCBMs on substrates consists of a sequence of discrete transformations of the molecules from one state (A) to another (B). Such a growth process can be likened to a simple Markovian walk [35], where the evolution of the state with time is governed by a master equation. Numerical solution to the master equation using kMC approach requires definition of key events, associated with individual deposition steps, and corresponding rates, k_{A-B}. The rates can be obtained from experiments, transition state theory, MD simulations or other schemes [34,36–43]. In this work, k_{A-B} of all elementary processes related to the deposition of PCBMs on perovskite surfaces during the growth of the monolayer were calculated from MD simulations. The MD simulations considered deposition of PCBMs, solvated in chlorobenzene (CB), on perovskite surfaces. A separate numerical algorithm was developed to obtain the rates for the most relevant events from these MD simulations. The kMC simulations employed the calculated rates in a stochastic framework and simulated the deposition of PCBMs on a much larger perovskite surface than that accessible to MD. Each processing condition was simulated at least 50 times to obtain statistically meaningful growth rates and morphological characteristics of the monolayer during deposition. Due to the inherent ability of the kMC method to scale up, the model can access the time required to cover a large surface, which is comparable to the size of surfaces used in experiments. Details of the MD and kMC methods applied in this study are provided below.

2.1. Molecular dynamics simulations

In order to define events related to the deposition and growth of PCBMs on perovskite substrates and calculate associated rates, we simulated dispersed PCBMs in CB solvent sandwiched between two perovskite crystal surfaces using MD. The distances between centers of mass of each PCBM and the surfaces were kept sufficiently large (at least ~1.5 nm) at the initial configuration of the simulated system to eliminate biased depositions. Fig. 1 shows a representative diagram of the system. The deposition characteristics are directly related to the crystal face, which is orthogonal to *z*-axis, on which monolayer growth occurs. We chose to simulate deposition of PCBMs on (110) face of tetragonal methyl ammonium lead iodide perovskite crystal, motivated by prior studies that have shown that the (110) crystal face contributes to long charge carrier life time and therefore improves the device performance of PSCs [44,45]. We varied the mass fraction of PCBM in the simulated systems in order to determine the effect of concentration of PCBMs on deposition and growth characteristics. The concentra-