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Towards Model-Guided Defect Reduction in $Cd_{1-x}Zn_xTe/CdS$ Solar Cells: Development of Molecular Dynamics Models

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***Abstract* — $Cd_{1-x}Zn_xTe/CdS$ solar cells are currently limited by material defects. While nano-structuring promises further defect reductions, the materials synthesis and characterization become more challenging. Molecular dynamics models capable of growth simulations enable defects to be explored without assumptions, and can therefore guide nanoscale experiments. Such models are difficult to develop, and are not routinely available in literature for semiconductor compounds. To fill this gap, we have developed growth simulation enabling Stillinger-Weber and bond-order potentials. These new models begin to enable molecular dynamics to be used to explore nano-structured $Cd_{1-x}Zn_xTe/CdS$ solar cells with reduced defects.**

***Index Terms* — CdTe, molecular dynamics, interatomic potential, photovoltaic cells, silicon.**

I. INTRODUCTION

Currently, the CdTe-based solar cells have the lowest cost (per watt electrical energy) as compared with any other photovoltaic technologies [1]. These solar cells can profoundly change energy supplies if the 17.3% energy efficiency achieved today is significantly improved towards the 29% theoretical value [2,3]. The under-achieved efficiency is attributed to charge trapping defects at the multilayer interfaces [4-6]. Nano-structuring can potentially remove these defects. However, this is not easy to achieve because material synthesis and characterization become increasingly difficult at smaller the scales. Molecular dynamics (MD) simulations track atom positions as a function of time from Newton's equations of motion, and as a result, can reveal defect formation without any assumptions. Such simulations can effectively guide nanoscale experiments for defect reduction, provided that accurate results are obtained. This essentially requires that a high-fidelity interatomic potential be used in MD to calculate interatomic forces. Here by high-fidelity we mean that the potential simultaneously satisfies two criteria: (a) captures property trends of a variety of equilibrium and metastable structures as determined from density function theory (DFT) calculations; and (b) predicts the crystalline growth of the lowest energy phases during MD vapor deposition simulations. The deposition simulations are extremely important because they simulate the synthesis by random adatom addition without any assumptions, and they test unlimited configurations formed on the growth surface that are unlikely to be tested otherwise. In particular, the simulations would incorrectly predict an amorphous growth if the potential prescribes any wrong structures to have a lower energy than the equilibrium substrate phase. Unfortunately, deposition simulations are not usually tested in past potential development. As a result, the "growth simulation enabling" potentials are not routinely available in literature, at least for semiconductor compound systems.

In our DOE project to improve $Cd_{1-x}Zn_xTe/CdS$ solar cells via nano-patterning and composition grading, we developed new, growth simulation enabling Stillinger-Weber (SW) [7] and bond-order [8-10] potentials. These models have begun to impact our experimental efforts in the same project [11].

II. THE STILLINGER-WEBER POTENTIAL

Due to its simplicity, SW potential is the most widely used semiconductor potential. We found that to enable growth simulations, the key for a multi-element SW potential is to capture exactly the experimental structures, lattice constants, and cohesive energies of all stoichiometric compounds, the experimental cohesive energies for the model elements, and the correct positive heat of mixing for all the non-stoichiometric alloys. The literature SW potentials that failed in the growth simulations are likely not fitted to these important properties. By fitting these properties, we developed a SW potential for the II-VI elements Zn-Cd-Hg-S-Se-Te [7]. This potential is successfully used in two stringent cases.

In the first case, MD simulation is used to grow a $(Cd_{0.28}Zn_{0.68}Hg_{0.04})(Te_{0.20}Se_{0.18}S_{0.62})$ super-alloyed compound layer on ZnS substrate, and the final configuration is shown in Fig. 1. Fig. 1 convincingly versifies that the MD simulation predicts a clean crystalline structure as expected from experiments, even when a variety of randomly disordered configurations involving six different elements are continuously initiated on the surface.

In the second case, MD simulation is used to grow ZnS/CdSe/HgTe multilayers, and the final configuration is shown in Fig. 2. Fig. 2 verifies that the MD simulation not only correctly captures the crystalline growth of the complicated semiconductor multilayers, but also reveals a variety of defects important to the solar cell properties, such as subgrains, stacking faults, dislocations, interstitials, antisites, interlayer mixing, and vacancies. The model, therefore, can be used to explore methods to reduce these defects [11].

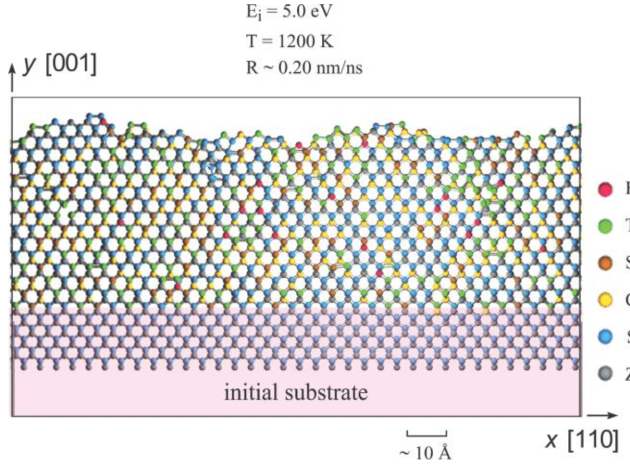

Fig. 1. MD prediction of $(Cd_{0.28}Zn_{0.68}Hg_{0.04})(Te_{0.20}Se_{0.18}S_{0.62})$ layer on ZnS. The pink shaded region highlights the initial ZnS substrate.

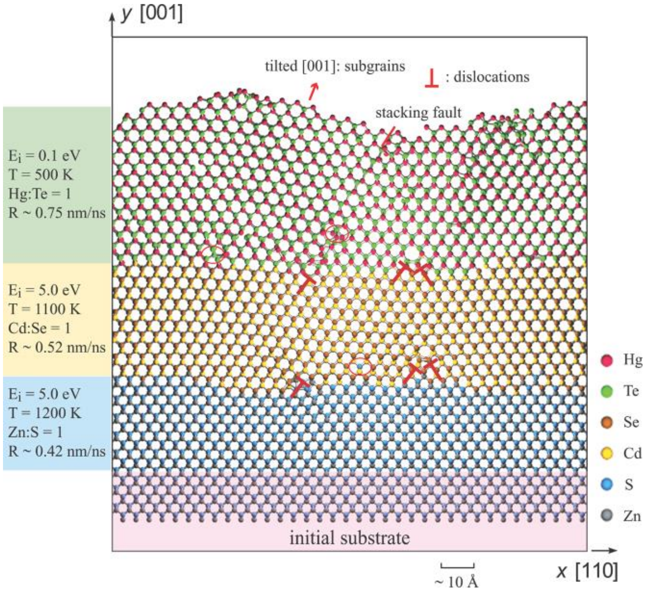

Fig. 2. MD prediction of ZnS/CdSe/HgTe multilayers on ZnS. The pink shaded region highlights the initial ZnS substrate.

II. THE BOND-ORDER POTENTIAL

To improve beyond the SW model, we have also developed a CdTe bond-order potential (BOP) [8-10]. The BOP here is derived from quantum mechanical theories by Pettifor and his colleagues [12-13]. Different from the empirical BOPs commonly referred to in literature, this BOP is currently only applied by few specialized groups. While Pettifor and his colleagues focus on BOP theories with some related parameterizations, we exclusively focus on BOP parameterization and applications. BOP parameterization is not trivial, and enormous iterations are required to develop growth simulation enabling BOPs. Nonetheless, well parameterized BOPs have been demonstrated to significantly improve over empirically-based potentials. To demonstrate, energy trends of different Cd, Te, and CdTe structures predicted by our BOP, DFT, a literature SW [14], and a literature Tersoff-Rockett (TR) [15] potential are compared in Fig. 3, along with the experimental data for the equilibrium phases.

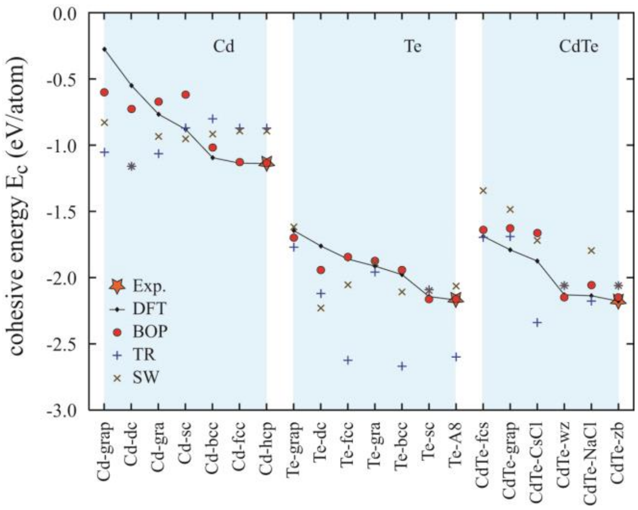

Fig. 3. Energy trends of different structures predicted by different models. The DFT data have been scaled to match the experimental data (red stars). The lines are used to guide eyes with no implication on any continuity of data.

Fig. 3 indicates that the literature TR potential cannot be applied to study either elements (Cd and Te) or compound (CdTe) because it does not give the lowest energy for the equilibrium phases indicated by the red stars. Note that this deficiency may come from parameterization, but not the potential format. While the literature SW potential also does not give the lowest energy for the equilibrium elemental phases (hcp Cd and A8 Te), it does give the lowest energy for the correct zinc-blende CdTe phase. Hence, it can be used to study CdTe. Contrarily, BOP predicts correctly the lowest energy phases for Cd, Te, and CdTe. In addition, the overall energy trends of BOP for a variety of other phases are much closer to the DFT data than those of the SW and TR potentials. This BOP, therefore, enable high-fidelity MD simulations of CdTe-based solar cells.

CdTe BOP model has been validated in numerous cases. Two cases are shown in Figs. 4 and 5 respectively. In Fig. 4, the BOP-based MD is used to simulate the growth of CdTe on GaAs [16], and the predicted atomic structures are compared with high resolution electron transmission microscopy (HRTEM) image obtained from literature [17]. It can be seen that the simulation not only achieves the crystalline growth, but also predicts similar misfit dislocation configurations (two extra planes about 145° from the vertical direction) and density to the experiments. This strongly validates the BOP model.

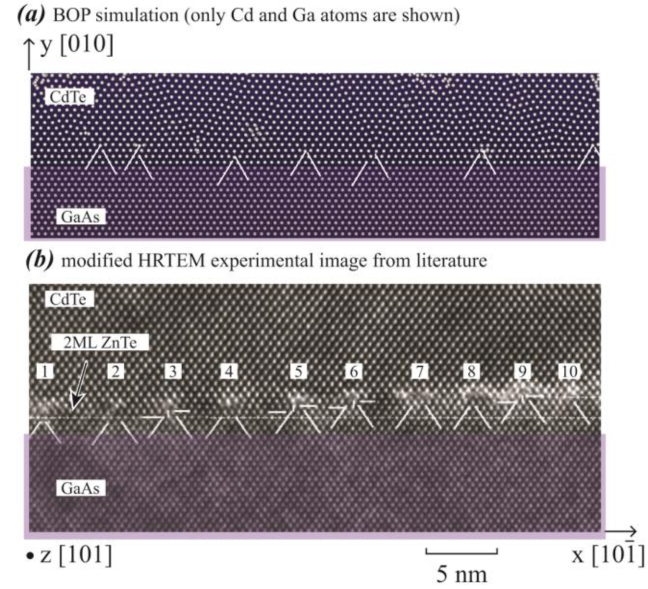

Fig. 4. Validation of BOP prediction on vapor deposited CdTe/GaAs films.

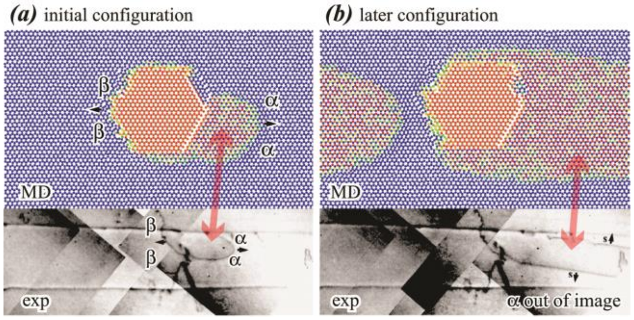

Fig. 5. Validation of BOP prediction on dislocation loop evolution under stress in semiconductor compounds.

In Fig. 5, the BOP-based MD simulation is used to study the evolution of a dislocation loop in a CdTe crystal under an external shear stress [18], and the results are compared with literature in situ HRTEM images [19]. It can be seen that the dislocation loop become a one-dimensional band in the simulation, in agreement with the experiments [19]. Referencing to the dislocation types indicated in the figure, this means that the simulation reproduces the well-known experimental observation in semiconductor compounds that α dislocations move much faster than β dislocations. The same phenomena were not observed when we use other potentials to perform the same simulation. Fig. 5, therefore, strongly validates that the BOP is a more advanced model.

III. DISCUSSIONS

With vapor deposition simulations as stringent verification tests, the atomistic models we developed open new ways to explore defect reduction in CdTe-based solar cells. Due to the short time scale of MD simulations, the vapor deposition simulations have to be performed at very high deposition rates as shown in Figs. 1 and 2. Correct interpretation of the MD results directly determines the impact of the approach. First, unlike kinetically trapped defects such as vacancies that are buried by fast deposited adatoms, the misfit dislocations are created from an originally dislocation free film due to strain relaxation. Such dislocations are correctly predicted despite the high deposition rates because they are more likely to form at low deposition rates when more relaxation time is available. This accounts for the agreement achieved between simulations and experiments shown in Fig. 4. Second, because a temperature increase around several hundred degrees can accelerate the kinetics by 10 orders of magnitude or more due to Arrhenius equation, the effects of fast growth rates can be mitigated by elevated temperatures. Third, the defects seen in MD simulations always exhibit the low energy configurations that are likely to occur in experiments despite the growth conditions. These defects can be used as inputs to further explore properties using DFT, which often cannot self-generate initial relaxed defects due to computational cost.

One effective use of MD vapor deposition simulations is to explore trends between structures and processing conditions. Note that the crystalline films are only obtained within a high temperature, low growth rate window in simulations. In particular, the high quality multilayers shown in Fig. 2 are not easy to achieve, requiring more than 10 iterations in simulations. Without the “in situ” computational visualization of the atomic structures and their formation mechanisms, experimental optimization of multilayer growth is far more difficult. However, insights gained during the computational synthesis may help guide the experiments. For achieving the quality shown in Fig. 2, the layers had to be grown in a sequence with decreasing melting point so that each layer can be grown at the highest temperature possible without melting the previous layer. The observation that the conditions optimized for the growth of each layer may destroy the previous layers is an important insight that needs to be considered during experimental synthesis.

The most effective use of high-fidelity atomistic models is to use them in molecular statics (energy minimization) simulations to create a large database for energies at various geometries, dimensions, and defect types and concentrations. Such a database allows the construction of analytical model to predict defect concentrations as a function of nanostructure dimensions. As an example, we have used the BOP to derive misfit dislocation density as a function of nano structure dimension of CdTe/CdS and ZnTe/CdS heterostructure. The results are shown in Fig. 6. Fig. 6 indicates that misfit dislocation density can be significantly reduced by decreasing the dimension, and dislocation free structures are obtained when the dimension is reduced to about 90 nm for the ZnTe/CdS and about 40 nm for CdTe/CdS heterostructure.

Such predictions have begun to motivate our experimental efforts towards a nanoscale regime that is not routinely achievable currently. The atomistic tool also plays an important role in diagnostics for probing the problems when experiments do not produce the expected results. These of course assume that the predictions are accurate. Extensive validation tests such as the ones demonstrated in Figs. 4 and 5 are effective to ensure the accuracy. One the other hand, the predicted defect-free structures can also be directly verified with BOP-based MD simulations.

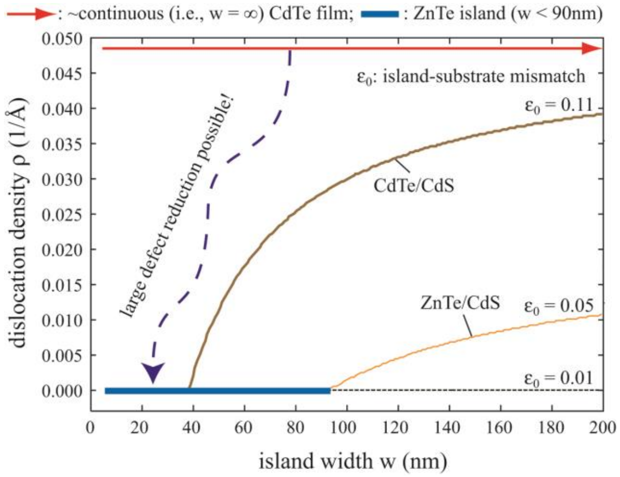

Fig. 6. BOP-based prediction on misfit dislocation density as a function of nanostructure dimension for CdTe/CdS and ZnTe/CdS heterostructure.

III. SUMMARY

New molecular dynamics models have been developed for Cd-Te and Cd-Zn-Te-S systems. These models are shown to be superior to the previous ones and can produce validated results to guide experiments for improving the CdTe-based solar cells.

IV. ACKNOWLEDGMENTS

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