Computational Methods for Amorphous Semiconductor Devices

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Abstract

- DOS
- structural modeling

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1. Introduction

1.1. Why model amorphous semiconductors?

1.2. How can we model amorphous semiconductors?

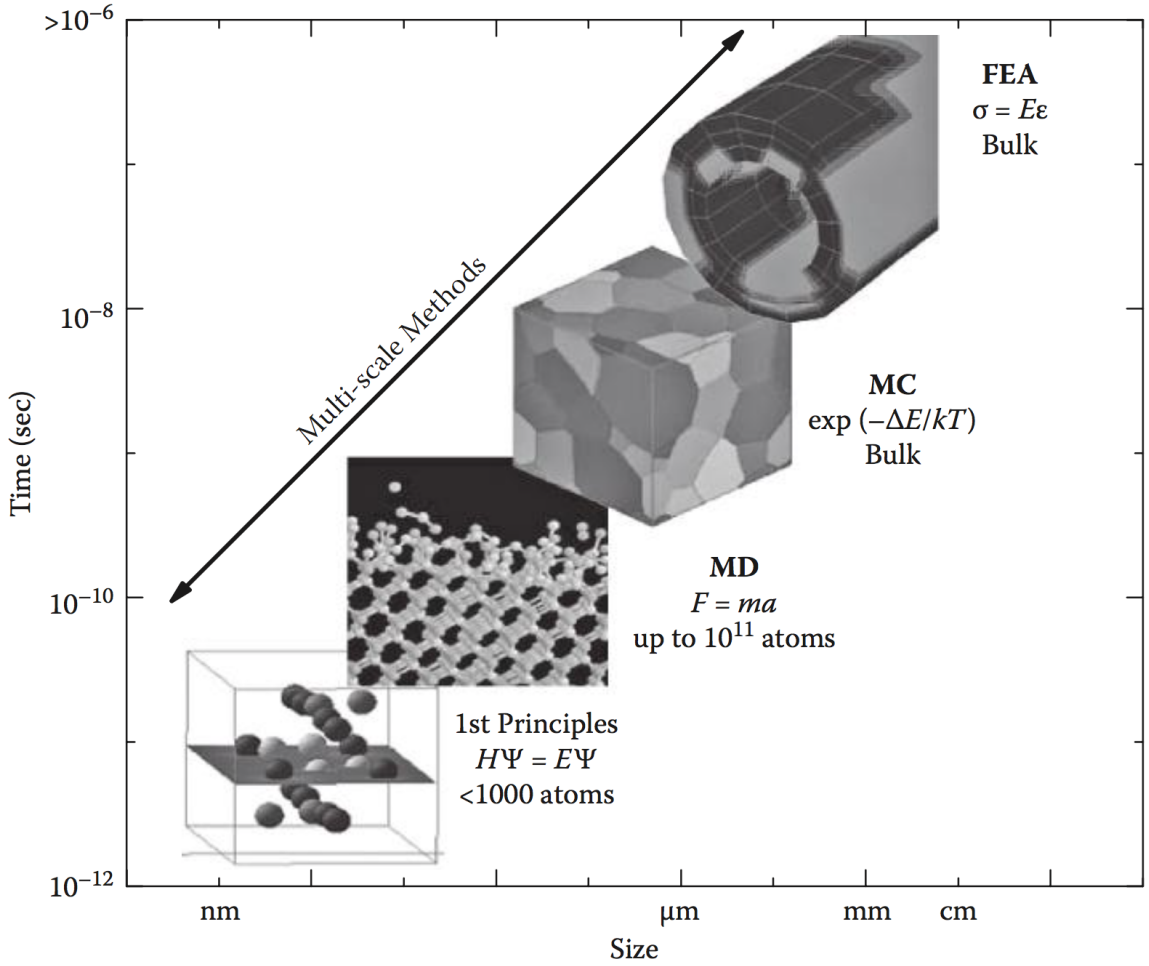

Figure 1: Overview of computational methods with respect to time and size capabilities.

2. Methods

2.1. Field Theory

2.2. Monte Carlo

2.3. Molecular Dynamics

2.4. Density Functional Theory

$$\hat{H} = -\frac{1}{2}\sum_{i}^{n}\nabla_i^2 - \sum_{I}^{N}\sum_{i}^{n}\frac{Z_I}{|r_{Ii}|} + \sum_{i\neq j}^{n}\frac{1}{|r_{ij}|} \tag{1}$$

$$\rho(r) = \sum_i |\phi_i(r)|^2 \tag{2}$$

2.5. Ab Intio Molecular Dynamics

Raty et al. [2] used Ab Initio Molecular Dynamics to understand the structural changes associated with aging in GeTe, and the effects those changes have on performance. Inherently out of equilibrium, amorphous materials evolve with time to a lower energetic state. In the case of phase change materials, this evolution leads to higher electrical resistivity that undermines its usability in multilevel memory devices. Using AIMD, we can watch the structure evolve, but though we discussed the addition of time to DFT above, this time is still on the order of picoseconds, leaving real-time aging out of the quesion. Raty et al. have sidestepped this problem by creating an arrangement of structures with varying local motifs.

Their study begins with the observation that AIMD simulations of $Ge_xSb_yTe_{1+x+y}$ alloys show tetrahedrally bonded Ge (Ge^T) atoms in the amorphous phase, though these are absent in crystalline Ge. To investigate the effect of such homopolar bonds on GeTe properties, the authors melt-quenched combination of other binary chalcogenides as "templates." SiTe forms numerous Si^T, GeSe contains some Ge^T, and SnTe contains almost no tetrahedral motifs. The authors then substituted one species in each of the template compounds to form GeTe, i.e. substituting Si in SiTe with Ge, Se in GeSe with Te, and Sn in SnTe with Ge.

Notes

- Kohn Sham: A *system* of one-electrons
- Hartree: a *potential* of how each electrons feels the electron gas
- Hartree Fock: how we describe the wave functions

2.6. AIMD

Hohl 1991[1] - Liquid and amorphous Se

Computational comments

- many structural models have been proposed and often conflict
- models based solely on small differences are insufficient to explain all measured features
- even carefully constructed empirical potentials have difficulty in highly anisotropic covalent systems such as group-IVA elements.
- AIMD avoids parameterization of interatomic forces common in MD

Raty 2015 [2] - Aging in Phase Change Materials (dots figure)

- Motivation
  - ”Amorphous materials are out of thermodynamic equilibrium”
  - subject to physical aging
  - phase-change materials (PCMs) have a fast, reversible switch between a conductive crystalline and more resistive amorphous phase
  - aging increases the resistivity - ‘resistance drift’
  - computer simulation to investigate relaxation processes
  - **Modeling comment:** complexity of the chemistry requires DFT to describe and understand bonding and the amorphous phase
- Literature
  - DFT simulations of GeSbTe alloys report many tetrahedrally bonded Ge, which does not exist in crystal. These are obtained from MQ calcs
- Methods
  - Car-Parrinello
  - **To circumvent time scale problem, generated collection of a-structures**
  - mixed Gaussian/plane wave code in CP2K

- cutoff 300 Ry
- sampled at gamma only
- annealed using plane-wave code in Quantum Espresso
- 34 Ry
- 3.84 fs
- Berendsen thermostat
- 10 models produced starting from liquid

• Results

- Ge^T is associated with homopolar Ge-Ge bonds
- heat of formaion shows homopolar bonds more favorable in GeTe than GeSe and SnTe
- wanted to investigate effects of varying amounts Ge-Ge bonds
- used different alloys along the phase diagram and substituted with Ge or Te to form different GeTe structures "mimicking aging"
- homopolar bonds correlated with tetrahedral Ge
- freezing at density of amorphous GeTe, tetrahedral rich models had the largest values of stress
- this agrees with experiments showing the drift of PCMS is accompanied by stress relief
- order parameter d_4/d_0 goes from tetrahedrally bonded Ge, Ge^T, to Ge^{III} and d_3/d_0 goes from Te^{II} to Te^{III}
- increase in band gap directly linked to decrease in homopolar bonds
- "melt-quenched model has a smaller band gap and possesses a (localized) mid-gap state"

References

[1] D. Hohl, R. O. Jones, First-principles molecular-dynamics simulation of liquid and amorphous selenium, Physical Review B 43 (5) (1991) 3856–3870. doi:https://doi.org/10.1103/PhysRevB.43.3856.
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[2] J. Y. Raty, W. Zhang, J. Luckas, C. Chen, R. Mazzarello, C. Bichara, M. Wuttig, Aging mechanisms in amorphous phase-change materials, Nature Communications 6 (7467) (2015) 1–8. doi:10.1038/ncomms8467.
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