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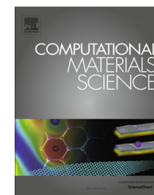

Gap tuning and effective electron correlation energy in amorphous silicon: A first principles density functional theory-based molecular dynamics study

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ABSTRACT

First principles density functional theory (DFT)-based molecular dynamics (MD) is used to study some physical and electronic properties of amorphous silicon (a-Si) samples, as-quenched and annealed containing dangling and floating bonds (pertinent to the threefold- and fivefold-coordinated defects, respectively) as well as distorted tetrahedral bonds. Surprisingly, except for the work of Pantelides (1986) who gave a rough estimate for the effective electron correlation energy, U_{eff} of a floating bond on the fivefold-coordinated Si, to date, there are no theoretical studies in the literature for the calculation of U_{eff} pertinent to this type of defect. In this work, U_{eff} for each type of defect, namely, threefold- and fivefold-coordinated atoms which are present in our generated annealed a-Si sample at 300 K is calculated by the current *ab initio* framework. We found that, U_{eff} for the fivefold-coordinated Si varies from +0.32 to +0.41 eV, whereas for the threefold-coordinated Si it ranges between −0.33 to +0.04 eV. The electronic, optoelectronic, and transport properties of a-Si semiconductors are directly influenced by gap tuning which in turn is controlled by the applied strains. The effects of temperature and strain on the mobility gap and the electronic density of states (DOS) for the a-Si samples are of particular interest. For the unstrained as-quenched and annealed samples at $T = 0$ K, the mobility gap is calculated to be equal to 1.42 and 1.47 eV, respectively; whereas, at $T = 300$ K these values change to 1.17 and 1.24 eV, respectively. At $T = 0$ K, for both samples under the uniaxial tensile strains below 0.070, the calculated mobility gap is about 1.4 eV which sharply decreases by applying strain beyond 0.070. As it will be seen, the gap regions for both the unstrained sample and the strained sample with $\epsilon_{33} = 0.070$ contain midgap states, but for the strained samples with the higher strains of $\epsilon_{33} = 0.140$ and 0.210 the midgap states disappear.

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1. Introduction

Amorphous silicon (a-Si) has been increasingly used in highly sensitive micro/nano-electromechanical systems (MEMS/NEMS); it is also suitable for usage as the substrate of electronic devices [1–3]. The principles of detection in some biosensors are based on the electronic and optoelectronic properties of a-Si. For example, in thin film a-Si light sensors the emitted light is converted into an electrical signal, thus allowing the optoelectronic detection of the DNA molecules. Whereas, in ion-sensitive thin film a-Si transistors the induced voltage shifts are the basis of detection for sensing of DNA and proteins [4–6]. The gap tuning technology in a-Si can control the accuracy of the functionality of these devices.

The electronic properties of a-Si is strongly influenced by its microstructure and the number of coordination defects. Tetrahedrally bonded a-Si semiconductors consist of inherent structural defects of threefold-coordinated atoms with a dangling bond [7–9], fivefold-coordinated atoms with a floating bond [10,11], and distorted tetrahedral bonds. Thus, a typical sample generated via some theoretical approaches should ideally contain all the mentioned inherent structural defects. However, a close scrutiny of the literature reveals that certain electronic phenomena associated with a-Si have been addressed in the absence of at least one type of the coordination defect. In continue as it will be discussed, the current work intends to study the phenomena of interest in the presence of all the inherent structural defects. An important parameter affecting the number of coordination defects is the thermal

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fluctuation which will also be accounted for in this work. More specifically, for the sake of the generation of the samples, we employ *ab initio* molecular dynamics (MD) in conjunction with Kohn–Sham density functional theory (DFT). In what follows, first we give a brief review of the theoretical generation of a-Si sample and then move on to discuss the electronic phenomena of interest undertaken in this work. Previously, some amorphous models containing both the threefold- and fivefold-coordinated defects were successfully generated based on classical many-body interatomic potentials [12–18] as well as *ab initio* MD employing tight-binding approximation [19–21]. Štich et al. [22] who simulated a-Si using a 64-atom cell on the basis of first principles DFT captured fivefold-coordinated defect only. They utilized norm-conserving pseudopotentials of the Bachelet–Hamann–Schlüter type for electron–ion interactions and the Γ point for the Brillouin zone (BZ) sampling. Fornari et al. [23] employing DFT in combination with accurate norm-conserving pseudopotentials and 8 **k** points in the full BZ prepared 64-atom a-Si sample consisting of both threefold- and fivefold-coordinated defects. They studied the extended nature of fivefold-coordinated atoms based on the decomposition of the electronic ground state into localized orbitals using the technique of maximally localized Wannier functions. The experimental circumstances of the preparation for a-Si films deposited by the pyrolytic decomposition of silane and plasma-deposited a-Si result in a significant percentage of hydrogen atoms bonded into the a-Si [24,25]. A recent work that has considered the effect of temperature on the fluctuation in the number of coordination defects is due to Drabold et al. [26], but it is pertinent to the hydrogenated a-Si. They concluded that this fluctuation serves as a mechanism for bond-center detachment in a-Si:H, liberating Hydrogen. Additives like Hydrogen has important role in the determination of the microstructure including voids, internal surfaces and even two-phase heterogeneities [27–29] as well as terminating dangling bonds [30] and the formation of light-induced metastable defects [31].

Anderson [32] and Street and Mott [33] when studying over-coordinated and under-coordinated defects of chalcogenide glasses and Kastner et al. [34], Adler [35], and Adler and Shapiro [36] when studying the electronic structure of a-Si in the presence of the dangling bond observed considerable atomic relaxations around the electrons of defect centers yielding localized states due to breaking down the one-electron and the conventional adiabatic approximations in such electrons. This phenomenon results in a strong electron–phonon (host network) coupling [32–36]. Drabold et al. [26] in their study on the thermally-induced coordination fluctuations in a 64-atom a-Si sample containing both types of the inherent structural defect argued that the electron states near the middle of the gap and tail states are strongly influenced by coordination fluctuations and illustrated that the electron–phonon coupling is always large for the localized states. Electron–phonon interaction yields an effective attraction between two electrons localized near the same defect center which can be described via the introduction of the effective electron correlation energy, U_{eff} [32,33,36,37]. Up to 1986, before the work of Pantelides [10] who gave a new perspective on the structural defects of a-Si, the dangling bond was commonly believed to be the dominant defect. Surprisingly, except for the work of Pantelides [10] who presented an approximation for U_{eff} of a floating bond on the fivefold-coordinated Si, to date, there are no theoretical studies in the literature for the calculation of U_{eff} associated with this type of defect.

The electronic density of states (DOS) is an extremely important concept for the study of the behavior of materials [38]. For example, most physical properties of semiconductors such as optical absorption, transport, electronic and optoelectronic properties are intimately dependent upon this parameter [39]. Joannopoulos and Cohen [40–42] calculated DOS and band structures of a series of structures representing amorphous germanium and amorphous silicon at absolute zero. Their amorphous models including face-centered cubic with 2 atoms per primitive cell (FC-2), hexagonal 2H with 4 atoms (2H-4), body-centered cubic with 8 atoms (BC-8), and simple tetragonal with 12 atoms per primitive cell (ST-12) were prepared using the empirical-pseudopotential method and the tight-binding model. In fact, the amorphous models were crystals with long-range order, while the atoms in the primitive cells of the crystals were in a disordered tetrahedral arrangement. Recently, Morishita [43] and Zhao et al. [44] have also examined the electronic DOS of 64-atom a-Si sample. Morishita [43] generated 64-atom samples of high-density and low-density a-Si using isothermal–isobaric first principles MD simulations. He examined the structural differences between high-density and low-density amorphous configurations and their influence on the electronic and vibrational DOS. Zhao et al. [44] presented the electronic DOS of the pure a-Si structure and lithiated a-Si using first principles calculations based on DFT. They generated their samples using 64 Si atoms with periodic boundary conditions; as they have reported the corresponding DOS of the pure a-Si structure shows semiconducting character with a clear gap between the occupied and unoccupied states.

The effects of temperature on the mobility gap and the electronic DOS which are among the concerns of the current study have been the subject of several works. The temperature dependence of electronic properties of a-Si was first studied by Drabold et al. [45] using *ab initio* MD – computer program of Sankey et al. [46,47] employing tight-binding approximation. In order to verify the experimental probes of the electronic DOS given by Aljishi et al. [48], Drabold et al. [45] simulated a 63-atom cell with 4 **k** points as well as a 216-atom cell of Wooten et al. [49] with the Γ point at 300 K. Drabold and Fedders [50] employed the relaxed versions of the a-Si supercell of Djordjevic et al. [51] and the approximate local basis *ab initio* MD scheme of Sankey et al. [46,47] at 300 K and concluded that the simultaneous presence of the topological and thermal disorder in a-Si influence the localized electronic states.

To date, the sensitivity of the electronic properties of a-Si samples including the details of the mobility gap region and the electronic DOS to applied uniaxial strain has not been addressed in the literature. Normally, due to deposition rate and deposition temperature of amorphous semiconductor film on to a substrate as well as the film-substrate interface effects, the film is subjected to strain which consequently alters its physical properties. Singh [39] has pointed out that the presence of uniaxial strain can improve the transport property of some devices.

In the light of the above-mentioned existing shortcomings on the electronic properties of a-Si containing both the threefold- and fivefold-coordinated defects, in the current work it is intended to address the following issues: (1) calculation of the effective electron correlation energy, U_{eff} of dangling and floating bonds (Section 3), (2) calculation of the electronic DOS and band structure at $T = 0$ and 300 K (Section 4), and (3) the effect of strain on gap tuning and the electronic DOS (Section 5). Afterwards, a summary and conclusion of the present work is given in Section 6.

2. Preparation of a-Si samples containing both the dangling and floating bonds

Thermal treatments like annealing time, observation time, and temperature rate are quite critical in the creation of dangling and floating bonds within the generated amorphous samples. For example, the thermal process applied in the *ab initio* generation of a-Si samples by Štich et al. [22] resulted in the formation of only

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