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# Electronic structure and optical properties of B/P-doped amorphous Si calculated by first-principles

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## ABSTRACT

In order to understand the electronic structures, optical properties, and explain the experimental observations of B/P-doped amorphous Si, the relevant micro-structure and properties have been calculated by simulated annealing and DFT+U methods. Based on the calculated results, the short-range order features of micro-structure in amorphous Si lead to the similar electronic structure and optical properties with crystalline Si, owing to the short-range order reflects the nature of atomic chemical bonding and plays a major role in the decision of fundamental characteristics of amorphous Si. What is important, the long-range disorder features of micro-structure lead to the different electronic structure and optical properties of amorphous Si, in compared with crystalline Si. Especially, the localized states caused by structural defects predominately determined the optical properties in visible-light region. The findings in the present work could well explain the experimental observations in literatures, and are helpful for the development of amorphous Si based functional materials.

## 1. Introduction

Recently, the hot-topic of solar cells is still developing the efficient, low-cost, and long-term stable key-materials. To further reduce the cost of solar cells, the technology of thin-film solar cells is increasingly emerging. Its incomparable advantages of low-cost include: significantly reduce material usage; using low preparation temperature to prepare; easy to manufacture large-area product. In recent years, thin film solar cell has received widespread attention and has achieved great development [1]. In a variety of thin film solar cells, the development of amorphous silicon (a-Si) based thin film solar cells is particularly interesting. a-Si and hydrogenated amorphous silicon (a-Si:H) thin films have attracted much more attention for use in uncooled microbolometers, solar cells, and medical apparatus, etc., due to its enhanced optical absorption, high temperature of resistance and compatibility with current Si-based semiconductor technology. Compared with other types of Si-based solar cells (including: crystalline silicon (c-Si), microcrystalline silicon (μc-Si), and polycrystalline silicon (pc-Si)), a-Si based thin film solar cells consume less silicon materials, so the manufacturing cost is much lower. Especially, a-Si could be deposited on the low-cost substrates, such as glass, plastic and stainless steel, which makes it more competitive in cost-control. Presently, a-Si based thin film solar cells are popular in the international market. Therefore, as an important photoelectric material in energy-information industry, a-Si based thin film solar cells with high efficiency, stability and low-cost are earnestly expected to replace c-Si based solar cells. However, the problems on the poor conductivity and stability of a-Si films are yet not ultimately resolved. Thus, the studies at present or in the future are to be carried out on preparing device-quality and long-term stability a-Si or a-Si:H films.

For the applications of a-Si thin film semiconductor technology, the ability to control the conductivity by impurity doping is one of the key processes. Because of a-Si and c-Si are quite different in the band structure and the micro-structure, so the doping mechanism is consequently different. Since 1975, Spear et al. achieved controllable doping for a-Si:H, a-Si based semiconductor devices are rapidly realizing practical, and the basic theory about a-Si therefore has a breakthrough [2]. Thereafter two decades, a large-area, low-cost of doped a-Si film is widely available in the p–n junction, Schottky barrier semiconductor device, photoelectric detection, and display devices. For example, light B-doped a-Si can be used as a near infrared detector the photosensitive layer [3]. Thin film solar cells is currently the most widely application field for a-Si. At 1976, Carlson et al. made the world's first a-Si based thin film

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solar cell, with an efficiency of 2.4% [4]. Generally, in the visible-light range of solar spectrum, the absorption coefficient of a-Si is higher than that of c-Si by an order of magnitude, and its intrinsic absorption coefficient is as high as $\sim 10^5\,\mathrm{cm}^{-1}$. Furthermore, its absorb peaks are much closed to the peaks of the solar spectrum. In compared with c-Si, a-Si as the absorber material for solar cells has the following unique advantages: low-cost materials and manufacturing process, large-scale production capacity, variety and versatile, and so on. However, its fatal drawback is the light-induced degradation effect (namely Staebler–Wronski effect, SWE): the dark current and photoconductivity of a-Si:H can be reduced significantly by prolonged illumination with intense light; however they could reverse on heating the samples to above 150 °C [5,6]. One of efficient methods of reducing the SWE is stacking one or more thinner layers of a-Si together with other materials to form a multi-junction solar cell.

Different with c-Si based solar cells, the typical device structure of a-Si based thin film solar cells is the p–i–n or n–i–p structure. Thus, to achieve p- and n-type conductivity by impurity doping is necessary. Boron is the first impurity doping for a-Si, which could form a shallow acceptor and acts as the p-type layer in p–i–n solar cells [7]. The internal electric field of a-Si solar cells is built by p-type and n-type layer, which directly affect the open circuit voltage and short-circuit current density of the solar cells. So, p- and n-layers that are formed by impurity doping play an important for the photovoltaic performance. Spear et al. found that the conductivity of a-Si can be controlled over many orders of magnitude by doping with substitutional B/P impurities, and therefore obtained p/n-type thin films [2]. Nowadays, with a-Si as the intrinsic absorption layer, doped a-Si as the p- and n-layer, a-Si based multi-junction solar cells have been successfully developed, and the photo-electric conversion efficiency is reaching to 13.4% [8].

Recently, Feldmann et al. found B/P doped a-Si layers act as carrier-selective contacts and lead to a significant reduction of the cell's recombination current. And they found that the excellent surface passivation could be achieved even for phosphorus implantations with high implantation doses. In contrast, B-doped c-Si shows poor surface passivation when anneal temperature is higher than 900 °C [9–11]. Using these p/n-type carrier-selective contacts of B/P-doped a-Si, they obtained a high photo-electric conversion efficiency of ~23%. However, the underlying mechanism, especially the reason for the degradation mechanism, is still not clear in their work. Furthermore, the formation mechanism and existing forms of structural defects induced by doping is a very complicated and important issue for a-Si. It is just the controllable doping that realizes the applications of a-Si. Therefore, the system investigation about defects in a-Si could provide an important theoretical basis for further explore the application of a-Si based material. Motivated by their experiment observations, we believed that it is necessary to systematically study the relationship between electronic structure and photovoltaic performance of B/P-doped a-Si, in order to develop efficient a-Si based thin film solar cells. Thus, in the present work, the micro-structure, electronic structure, and optical properties of B/P-doped a-Si were preliminary investigated by using density functional theory (DFT) calculations. Moreover, the relationship between electronic structure and photovoltaic properties will be discussed and compared. Based on the calculated results, possible explanations for previous experimental observations will be provided.

## 2. Computational methods and models

Cubic Si with the symmetry of $Fd\bar{3}m$ and the lattice constant of 5.4307 Å was adopted as the c-Si model. For crystalline cases, a $3 \times 3 \times 3$ supercell was used for constructing the B/P-doped c-Si models, in which one Si atom was replaced by a B or P atom. In these supercells, the total number of atoms is reached to 216. And then, the geometry of these supercells will be optimized by CASTEP code (the detailed method will mentioned as following). For the amorphous cases, the simulated annealing method to construct a-Si and B/P-doped a-Si models. The simulated annealing method uses a canonical Monte Carlo sampling of the search space during with the temperature was gradually decreased, which is a metaheuristic algorithm for locating a good approximation to the global minimum of a given function in a large search space [12,13]. In the present work, the Forcite code was adopted, which is implanted in Materials Studio 6.0. And this process was repeated to identify further local energy minima. During the course of simulation, atoms were randomly rotated and translated in a cubic box with 16.0769 Å. The configuration that results from one of these steps was accepted or rejected according to the selection rules of the Metropolis Monte Carlo method. In the computational parameters of Monte Carlo simulations, the universal force field was utilized to deal the atomic interaction, the force field form and parameters were adopted in Refs. [14–17] as following:

$$
\begin{aligned}
&E = E_R + E_\theta + E_\phi + E_\omega + E_{vdw} + E_{el} \\
&E_R = \frac{1}{2} k_{IJ} (r - r_{IJ})^2 \\
&E_\theta = K_{IJK} \sum_{n=0}^{m} C_n \cos n\theta \\
&E_\phi = K_{IJKL} \sum_{n=0}^{m} C_n \cos n\phi_{IJKL} \\
&E_\omega = K_{IJKL} (C_0 + C_1 \cos \omega_{IJKL} + C_2 \cos 2\omega_{IJKL}) \\
&E_{vdw} = D_{IJ} \left\{ -2 \left[ \frac{\chi_{IJ}}{\chi} \right]^6 + \left[ \frac{\chi_{IJ}}{\chi} \right]^{12} \right\} \\
&E_{el} = 332.0637 (Q_i Q_j / \varepsilon R_{ij})
\end{aligned}
\tag{1}
$$

In which, $E_R$ is the bond stretching interaction, $E_\theta$ is the bond angle bending interaction, $E_\phi$ is dihedral angle torsion interaction, $E_\omega$ is the inversion interaction, $E_{vdw}$ is the nonbonded interaction, and $E_{el}$ is the electrostatic interaction. The force field parameters are listed in Table 1. In addition, the charges of atoms were assigned by force field; the summation method was chosen as Ewald method; the cutoff distance was chosen as 15 Å; the number of cycles was chosen as 10, with $10^5$ steps per cycle; and the simulated annealing temperature cycle was determined automatically by the calculation package (maximum temperature is $10^5$ K, final temperature is 100 K). By this way, pure and B/P-doped a-Si models could be obtained, in which the total number of atoms is also reached to 216.

All of the calculations were carried out by using the periodic density functional theory package of Cambridge Serial Total Energy Package (CASTEP) codes [18]. CASTEP is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. The core electrons (B: [He], Si: [Ne], P: [Ne]) were treated with the ultrasoft pseudopotential. The exchange–correlation effects of valence electrons (B: $2s^2 2p^1$, Si: $3s^2 3p^2$, P: $3s^2 3p^3$) were described by the revised

**Table 1**
The parameters of universal force filed in Eq. (1).

| Atom type | Valence | | Nonbond | | | Effective charge: $Z_I^*$ (Charge) |
|---|---|---|---|---|---|---|
| | Bond: $r_\mathrm{I}$ (Å) | Angle: $\theta$ (°) | Distance: $\chi$ (Å) | Energy: $D_I$ (kcal $\mathrm{mol}^{-1}$) | Scale: $\zeta$ | |
| B | 0.838 | 109.47 | 4.083 | 0180 | 12.052 | 1.755 |
| Si | 1.117 | 109.47 | 4.295 | 0.402 | 12.175 | 2.323 |
| P | 1.056 | 109.47 | 4.147 | 0.305 | 13.072 | 2.863 |