Mechanically Strengthened Amorphous Silicon by Phosphorus: A Molecular Dynamics Simulation and Experimental Study

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**Abstract:** The effects of phosphorus (P), one of the most common impurities in silicon(Si), on the mechanical responses of amorphous Si (a-Si) have been investigated numerically and experimentally. Tensile behaviors of P doped a-Si films were investigated using classical Molecular Dynamics(MD) simulations prescribed by Modified Embedded Atom Method(MEAM) formalism. The validity of this potential was verified by comparing our simulation results with accessible higher level calculations and experimental data. By conducting uniaxial tension simulations, it was revealed that the stiffness, yield strength and flow stress of bulk P-doped a-Si are increased, and that the ductility of a-Si film is evidently enhanced by P. Two factors account for this observation. One goes to larger bond strength of P-Si than that of Si-Si, and the other is the higher compactness of a-Si after introducing P impurities, both of which are in good agreement with experiments. Nanoindentation technology was applied to acquire the knowledge about how P impurities influence the indentation responses of a-Si. We observed a larger stiffness and stronger resistance to nanoindentation destruction as the concentration of P grew, consistent with MD conclusions though the enhanced ductility from MD calculations needs further work to verify.

1. Introduction

Pure elementary silicon(Si) when doped with traces of elements such as phosphorus(P) is an important semiconductor material, which has been extensively applied in high-tech industries like integrated circuit(IC), micro/nano-electro-mechanical systems(MEMS/NEMS), solar cells and so on. Besides, as a representative covalent material, it is attractive in fundamental physics. Amorphous silicon(a-Si) has gained wide interests in the past decades because of low material consumption and flexible application\cite{1, 2}. Recently, a-Si has drawn intense attention as the potential anodes materials of the next generation of lithium cells. The mechanical failures of a-Si based micro-structures, like high acceleration shock, cycling loading failure, etc. have severely constrained its application\cite{3, 4}, which require delve deeper to figure out the underlying mechanisms and corresponding improvements.

Doping with foreign atoms is an effective way to modify materials properties\cite{5, 6}. The roles that dopant P plays in the failures of a-Si structures is worth studying theoretically and experimentally. However, experiments about the effects of P on the mechanical properties of a-Si are inaccessible in published references. Actually, experiments sometimes yield contradictory results owing to complicated experimental conditions. Take crystal silicon as an example, Cook et al.\cite{7} reported that heavy P doping at a level of $10^{18}$-$10^{19}$cm\textsuperscript{-3} exhibited no clear influence on the
fracture toughness of Si, and Nagy et al.[8] showed that ion implanted P increased the Young’s modulus of single crystal Si, while Zeng et al.[9] declared that the fracture toughness and Young’s modulus were, respectively, increased and decreased by heavy P doping at ~5×10^{19} \text{cm}^{-3}. Therefore, to clarify the underlying mechanism, insight into the microcosmic structural evolution is necessary. To this end, computational methods have provided an excellent option.

Density functional theory (DFT) and molecular dynamics (MD) are currently the most extensively used computational techniques. DFT provides more reliable information, which, however, is incapable of dealing with a thousand-scale system despite the rapid development of computer technologies. (Semi-)Empirical potentials have developed enormously in recent decades and enable simulations for million-level systems within classical force fields. But the reliability of MD results largely depends on the interatomic potentials. Therefore, simulations based on classical MD require direct or indirect validation from higher level calculations or experiments.

In this research, our recently developed potential was used to investigate the effects of P on the tensile mechanical responses of a-Si. Besides, to clarify the credibility of simulation results, a feasible experimental technique, i.e. nanoindentation test, was applied to supply side proof.

2. Effects of P doping on the mechanical response of a-Si

2.1 Numerical implementation

In (2NN) MEAM formalism, the total energy of a system is calculated in the following equation:

\[
E = \sum_i \left[ F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi(R_{ij}) \right]
\]

(1)

where \( F_i(\bar{\rho}_i) \) is the embedding function, \( \bar{\rho}_i \) is the background electron density at site \( i \), and \( \phi(R_{ij}) \) is the pair interaction between atoms \( i \) and \( j \) at a distance \( R_{ij} \).

We used Lee’s 2NN MEAM parameter set[10] for pure Si as it predicts relatively better physical properties of a-Si than the other empirical potentials. 2NN MEAM potentials for pure P and Si-P binary system were developed in our recent work[11]. In order to produce a reliable potential to describe Si-P compounds, a variety of fundamental properties were considered, including cohesive or formation energies, lattice constants and elastic constants of typical Si-P structures, point defects and P-vacancy pairs. All the calculations in present work were performed with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[12].

Two types of specimens were prepared for tensile tests of a-Si, namely bulk models and films. Correspondingly, the periodic boundary conditions (PBC) were applied in three dimensions for the former, and \( x \)-, \( z \)-dimensions for the latter. Loading directions are all along \( x \)-dimension at constant strain rate of 5×10^{8} \text{s}^{-1}. All the tensile tests were conducted at constant temperature 300K and pressure 1bar by means of Nosé-Hoover thermostat[13] and Parrinello-Rahman pressostat[14], i.e. NPT ensemble. In all cases, before loading, the models were relaxed for 100ps to remove the stresses that could develop due to thermal expansion. The time step was set 0.002ps.

2.2 Model Preparation

To create bulk a-Si, two phases of simulated annealing were performed under the NPT ensemble, during which the periodic conditions were applied in all orientations. First, a crystal sample with the length scale of 65.17Å×65.17Å×65.17Å and 13824 atoms was generated. Before
annealing Si atoms were replaced by P atoms according to different concentrations. The system was
heated rapidly from 300K to 4000K at the rate of 50K/ps and kept for 300ps, then quenched to
1250K at the rate of 2K/ps, and from 1250K to 750K at the rate of 0.1K/ps, finally from 750K to
300K at the rate of 1K/ps. The purpose of the second annealing was to release residual stress. The
system was heated to 1000K at the rate of 20K/ps, kept for 200ps, then decreased to 300K at the
rate of 2K/ps. During the first annealing, the cooling rate from 1250K to 750K was much slower
because the glass transition temperature $T_g$ of Si is about 1000K[15], around which the cooling rate
has great influence on the mechanical properties of a-Si or polycrystalline Si[16, 17].

The preparation of a-Si films followed the procedure of ‘melt-quench-duplicate’, as introduced
in literatures [18-20]. Bulk a-Si obtained above was reproduced and expanded along $x$, and
non-periodic condition was applied in $y$-orientation. Then the system was relaxed for 200ps at 300K
and 1bar, so that the surface atoms can be reorganized sufficiently. The whole process is shown in
Figure 1. Because of enormously high computational cost, only three concentrations were
considered, namely 0%, 3.125% and 6.25%. The size and number of atoms were respectively
195.87Å×65.29Å×65.29Å and 41472, 193.59Å×64.53Å× 64.53Å and 41472, 191.91Å×63.37Å× 63.37Å and 41472. The larger length scale along $x$ was due to the shear band of amorphous
structures that might happen when exposed to tensile stresses, which was not observed.

![Figure 1. Preparation process of a-Si films.](image)

2.3 Numerical Validation

The reliability of numerical investigation using (semi-)empirical potential needs validation. Usually, one can compare the computed typical physical properties with high level computations
and experiments. Table 1 lists the volume ratio at stable state, $V_a/V_c$, the bulk modulus of a-Si, $B_a$,
the bulk modulus of c-Si, $B_c$, and the difference of the two phases, $B_c−B_a$. These values obtained by
MEAM potential were calculated under 300K and 1bar, in accordance with experimental
conditions, while those from first principle calculation were obtained by fitting energy curves using
Murnaghan’s equation[21], which was equivalent to 0K and 0bar. $V_a/V_c$ and $B_c$ by MD are
remarkably comparable to experimentally obtained ones. $B_a$ predicted by MEAM is in satisfying
agreement with reference [22] and $(B_c−B_a)$ is within the range of experimental values.
Table 1. Structural parameters obtained in our calculations and experiment: The volume ratio of a-Si at stable state, \(V_a/V_c\), the bulk modulus of a-Si, \(B_a\) (GPa), the bulk modulus of c-Si, \(B_c\) (GPa), and the difference of the bulk modulus between c-Si and a-Si, \(B_c - B_a\) (GPa).

|                  | First principle calculation[21] | Experiments               | MEAM                |
|------------------|---------------------------------|---------------------------|---------------------|
| \(V_a/V_c\)     | 1.042                           | 1.017~1.019[23]           | 1.012               |
| \(B_a\)         | 61.27                           | 36~60[24]                 | 89.21               |
| \(B_c\)         | 89.59                           | 97.6[25]                  | 99.00               |
| \(B_c - B_a\)   | 28.32                           | 2~62[22, 24]              | 9.79                |

In order to confirm that the amorphous structure can be reasonably well described, the radial distribution functions (RDF) was calculated, and compared with corresponding first-principles calculation data, as shown in Fig. 2.

We failed to access to quantities in any publications or reports about above mentioned properties of P doped a-Si. Thus accordingly experiments have to be performed to validate numerical results indirectly or partially.

2.4 Simulation Results and Discussion

The stress-strain curves for bulk a-Si of three concentrations are plotted in Fig. 3(a). The stress-strain relationship exhibits the typical characteristics of metallic materials, namely partially linear at low strain range followed by a non-linear portion. It is evident that the stiffness, yielding strength and flow stress of bulk a-Si are increased by P doping. The qualitative results are given in Table 2.
Figure 3. Effects of P concentration on the tensile properties of (a) bulk a-Si and (b) a-Si films.

Table 2. Mechanical properties of bulk a-Si when doped with dopant P, including Young’s modulus, maximum stress, flow stress below 0.3 and above 0.3.

| Model    | Young’s modulus (GPa) | $\sigma_{max}$ (GPa) | $\sigma_{flow}(\varepsilon<0.3)$ (GPa) | $\sigma_{max}(\varepsilon>0.3)$ (GPa) |
|----------|-----------------------|----------------------|--------------------------------------|--------------------------------------|
| Pure     | 112                   | 9.57                 | 7.71                                 | 6.08                                 |
| 3.125%   | 130                   | 10.58                | 8.55                                 | 7.29                                 |
| 6.25%    | 201                   | 11.93                | 9.97                                 | 7.99                                 |

The tensile curves for a-Si are shown in Fig. 3(b). Only two concentrations were considered due to extremely high computation burden. One can see that pure a-Si film is brittle within the description of MEAM potential, and that dopant P largely enhances the ductility of a-Si film. Two factors might be taken into account. First, the MEAM calculated bond strengths of Si-P(371.09kJ/mol) is larger than Si-Si(302.99kJ/mol), consistent with experimental values, ~363.6kJ/mol for Si-P and ~325kJ/mol for Si-Si, respectively. Second, the atoms in P doped model are more close-packed than those in pure a-Si, which means the coordination number is increased by introducing P impurities, making it consumes more energy to generate regional micro voids. Besides, when micro voids come into being, nearest P atoms would impede their nucleation and propagation.

3. Effects of P on the nanoindentation responses of a-Si

As for tensile tests, the preparation and testing of a-Si films can only be carried out in the vacuum environment. Limited to this harsh condition, we had to apply nanoindentation tests to investigate the effects of P on the mechanical properties of a-Si.

3.1 Preparation of P doped a-Si

The a-Si films doped with P were processed by the plasma enhanced chemical vapor deposition (PECVD) technology. The ratios of PH3/SiH4 for the two groups of samples were respectively 0.5% and 1.5%, which were supplied by hina company. The processing conditions, such as discharge power, substrate material, ambient temperature and pressure, can impose strong influences on the mechanical and electrical properties of a-Si. The technological parameters used in this paper were: discharge power 90W, TCO glass for substrate glass, ambient temperature 150°C, and pressure 100Pa.
Fig. 4 presents the atomic force microscope (AFM) of two samples (measured by Dimension Icon atomic force tester of Bruker Inc.). Because of large surface roughness of a-Si, the scanning accuracy was lowered in order to protect the AFM probe, but without affecting the analysis. It is easy to observe the refined grains on surface and slightly reduced surface roughness (~67nm and ~51nm respectively) as the concentration grows.

![Figure 4](image1)

Figure 4. Surface morphologies of the a-Si samples with concentrations of (a) 0.5% and (b) 1.5%.

A-Si could recrystallize during the PECVD process, as some alien element such as hydrogen can promote the order of short range. In order to investigate the degree of recrystallization, the XRD curves were measured by X-ray diffraction instrument from WAVETEST Inc. Fig. 5 shows the XRD curve of the sample with lower concentration. Because dopant P can impede a-Si from recrystallization[26], the samples with higher concentration were not tested. We can see that the peak is located at 23° and wide enough, indicating that there is some kind of order in aSi, but there are no obvious diffraction peaks at the positions where the crystal structure of diamond is characterized by 28° or 47° or 56°, which means that the recrystallization is not obvious.

![Figure 5](image2)

Figure 5. XRD curve of a-Si with the concentration of 0.5%.

### 3.2 Nanoindentation Test

The nanoindentation tests were carried out with Acoustic Enclosure nano-indentation tester supplied by CSM Inc. The indenter was a Vickers indenter. The step rates of loading and unloading were both 10mN/ min. The maximum load was set 5mN because the a-Si films were thin, only a few microns. Fig. 5(a) exhibits the nanoindentation tester and sample clamping.
Fig. 5 compares the load-displacement curves of two samples with different concentrations. There is no observable discontinuity known as pop-in and pop-out on the curves, indicating that the recrystallization is insignificant. With the same indentation depth, the indentation load of the sample with higher concentration is larger than that of the other sample, which shows that the former has higher stiffness. The horizontal parts at the top of the curves indicate that the indenter rested for 10s when loaded to 5mN, and the depth continued to increase, indicating obvious creep in the samples. It can be seen that the creep amount of the sample with high phosphorus concentration is smaller, which indicates that the strength of amorphous silicon can be enhanced by impurity phosphorus to a certain extent. When the indenter is withdrawn, the pressure of the high concentration specimen returns to zero at the 120nm depth (the residual indentation depth), while the residual indentation depth of the low concentration sample is 160 nm, which indicates that the damage of the lower concentration specimen is more severe and the strength of the higher concentration sample is higher.

It’s noteworthy that hydrogen (H) was unavoidably introduced into a-Si samples during the fabrication process. Unfortunately, we failed to refer to related publications or reports about how H influences the mechanical properties of a-Si, which need further investigation.

4. Summaries

In summary, we have performed MD simulations and indentation tests to investigate how dopant P influences the mechanical properties of a-Si. The results are summarized as follows:

(1) From the perspective of MD, the stiffness, yielding strength, and flow stress of bulk a-Si are increased by P doping, mainly owing to larger bond strength of Si-P than that of Si-Si. A transition from brittle to ductile of a-Si film after introducing P can be observed.

(2) Nanoindentation responses of a-Si films with two different P concentrations were tested and compared. It is found that the stiffness of amorphous silicon films increases with the increment of P concentration. With the same indentation depth, the sample with higher concentration takes smaller damage and larger force, indicating that it exhibits greater material strength, which is consistent with MD simulations. As for the ductility transformation when introduced P, further work is needed to verify.
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