

## Interstitial-based boron diffusion dynamics in amorphous silicon

Ning Kong,<sup>1,a)</sup> Taras A. Kirichenko,<sup>2</sup> Gyeong S. Hwang,<sup>3</sup> and Sanjay K. Banerjee<sup>1</sup>

<sup>1</sup>Microelectronic Research Center, University of Texas at Austin, Austin, Texas 78758, USA

<sup>2</sup>Freescale Semiconductor, Inc., 3501 Ed Bluestein Boulevard, Austin, Texas 78721, USA

<sup>3</sup>Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, USA

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Using density-functional theory calculations we identified an interstitial-based fast boron diffusion mechanism in amorphous silicon. We found that interstitial-like point defects, omnipresent in as-implanted silicon, to be very stable in an amorphous network and can form highly mobile pair with Boron atoms. The transient existence of such point defects in amorphous silicon is suggested to play an important role in boron diffusion. We found the activation energy for this pathway to be 2.73 eV, in good agreement with experimental results. In addition, this mechanism is consistent with the experimentally reported transient and concentration-dependent features of boron diffusion in amorphous silicon. © 2008 American Institute of Physics. [DOI: 10.1063/1.2976556]

Preamorphization and solid-phase-epitaxial regrowth (SPER) techniques are widely used for silicon (Si) transistor fabrication. This approach can produce ultrashallow and steep junction profiles as well as high dopant activation level. However recently, Jacques *et al.*<sup>1</sup> reported five orders of magnitude boron (B) diffusivity enhancement in *a*-Si compared to that in crystal Si(*c*-Si) during SPER at 550 °C. Venezia *et al.*<sup>2</sup> and Duffy *et al.*<sup>3</sup> confirmed this high diffusivity and estimated the activation energy to be ~2.1 eV in *a*-Si, which is well below the value of ~3.65 eV in *c*-Si.<sup>4</sup> This abnormally fast diffusion in *a*-Si could cause significant B redistribution during SPER and thus poses a great challenge to ultrashallow junction formation. Despite the technological importance of this phenomenon, it is poorly understood. A recent experimental study<sup>5</sup> found this fast B diffusion to be transient and proposed a dangling-bond (DB)-mediated diffusion mechanism to explain it. Other theoretical studies<sup>6,7</sup> indicated that point defects, such as interstitials and vacancies which act as the major diffusion drivers in *c*-Si, also exist in *a*-Si. Urli *et al.*<sup>6</sup> also pointed out that the annihilation of point defects proceeds at the same pace as the DB reduction, which is consistent with the transient feature of this fast B diffusion. Therefore, in addition to the DB-mediated mechanism, point defects may also play a key role in the fast B diffusion in *a*-Si, especially when the implantation-induced point defects have a time-dependent high concentration before the structural relaxation in *a*-Si is completed. However, at this time, there is a little atomistic level understanding of dopant-point defect dynamics in *a*-Si.

In this letter, we examine B diffusion dynamics in *a*-Si using density-functional theory (DFT) and *ab initio* molecular dynamics (MD) simulations. Based on MD, we suggest an interstitial-based B diffusion mechanism in *a*-Si. The stability and migration barrier of the neutral and charged diffusion species are estimated. We propose an explanation for the high B diffusivity in *a*-Si, and compare our calculations with experiments.

A continuous random network model is used to generate a 64 atoms *a*-Si structure. The detailed procedure of *a*-Si construction can be found in Ref. 7. In most of our simula-

tions, the *a*-Si lattice undergoes no major structural change during the time scale in which B diffuses and interacts with point defects. Therefore this original *a*-Si structure is used as a reference lattice to show the B behavior. However, during this time scale, our MD simulation shows that if a Si atom is displaced from its original site, it will be mobile enough to diffuse around the relatively stable *a*-Si lattice and interact with B. We refer to this Si as “interstitial in *a*-Si” due to its similarity with interstitial in *c*-Si during the time scale in which B-point defect interaction occurs in this paper. On a larger time scale, this “interstitial” may not be distinguishable due to the entire *a*-Si structural relaxation and incorporation of this extra atom into the *a*-Si network.

For all calculations, we use the plane-wave basis pseudopotential method within the generalized gradient approximation to DFT, as implemented in the Vienna *ab initio* simulation package (VASP).<sup>8</sup> We use ultrasoft Vanderbilt-type pseudopotentials<sup>9</sup> and a plane-wave cutoff energy of 150 eV for MD and 250 eV for static calculation. All atoms were fully relaxed using the conjugate gradient method with force convergence threshold of  $1 \times 10^{-2}$  eV/Å. A  $(4 \times 4 \times 4)$  Monkhorst–Pack Brillouin zone sampling is used in the interstitial formation energy calculation while for other cases  $\Gamma$  point sampling is used. The temperature of MD simulation is controlled by the Nosé algorithm. A velocity Verlet algorithm was used for integrating the equations of motion with a 1 fs time step. Migration barriers are extracted using the nudged elastic band method (NEBM).<sup>10</sup> For the charged defect calculation, the overall charge neutrality in the periodic supercell is maintained by introducing a homogeneous background charge. The formation energy of positively charged defects relative to the neutral state is expressed as  $E_f^+ - E_f^0 = (E_D^+ - E_D^0) + (E_V + E_F)$ ,<sup>11</sup> where  $E_D$  is the total energy and  $E_F$  is the Fermi level relative to the valence band top,  $E_V$ .

Due to the lack of global symmetries in *a*-Si structure, the formation and migration energies of point defects and dopant species are heavily influenced by local environment, such as neighboring atomic and bond configuration, leading to relatively large variations. Therefore, we focus our study on extracting physical diffusion mechanism rather than finding exact energy values. Nevertheless, we try to minimize this variation by performing calculations at several locations

<sup>a)</sup>Electronic mail: kongning@mail.utexas.edu.

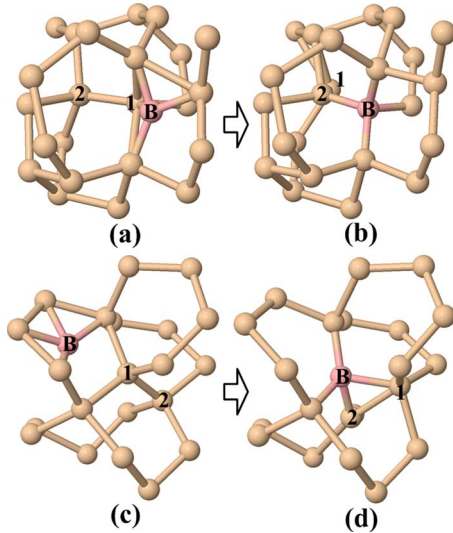


FIG. 1. (Color online) MD simulation shows that  $B_i$  will kick out lattice Si and becomes  $B_{\text{sub}}+I$ .

in the  $a$ -Si lattice. Our calculations indicate that B-vacancy pair is much less stable than B-interstitial pair in  $a$ -Si. Therefore, we consider only the behavior of  $B_i$ , where B is in an interstitial position among the original  $a$ -Si lattice sites, and  $B_{\text{sub}}+I$ , where B is in one of the original  $a$ -Si lattice sites with a neighboring Si displaced from this lattice site.

First, we observe the  $B_i$  dynamics in  $a$ -Si by performing MD simulation of a 900 °C, 2 ps anneal. We construct 19 initial  $a$ -Si+ $B_i$  structures, including 12 with  $HB_i$ , in which B is located in the center of a hexagonal ring, as shown in Figs. 1(a) and 1(c), 4 with split  $B_i$ , in which B shares a lattice position with a Si atom, and 3 with  $PB_i$ , in which B is in the center of a pentagonal ring, as shown in Fig. 2(b). After anneal, we find that in 14 out of 19 samples, the  $B_i$  kicks out a lattice Si and becomes  $B_{\text{sub}}+I$ . As shown in Figs. 1(a)–1(d),  $B_i$  kicks out Si 1 and takes the lattice position. By analyzing bond configuration changes and energy gains, we can clearly differentiate between  $B_{\text{sub}}$  and  $B_i$  in  $a$ -Si. The average energy gain from the initial state  $B_i$  to the final state  $B_{\text{sub}}+I$  is calculated to be  $0.56+0.26$  eV. The time evolution shows that  $B_i$  tends to occupy a lattice position in an early stage of the anneal and stays trapped until the end of the simulation. This trend indicates that B prefers to stay in the original  $a$ -Si lattice sites as  $B_{\text{sub}}$ , which may be due to charge transfer and local stress compensation effects.<sup>12</sup>

Due to the limited time period of MD simulation and the trapping efficiency of the  $B_{\text{sub}}$  state, it is difficult to capture long distance  $B_i$  jumps through  $a$ -Si lattice. However, we do observe this jumping in two of our samples, where a locally less-dense area is available between two interstitial sites so that  $B_i$  can migrate over with low barriers. This locally less-dense area possibly results from the inhomogeneous nature

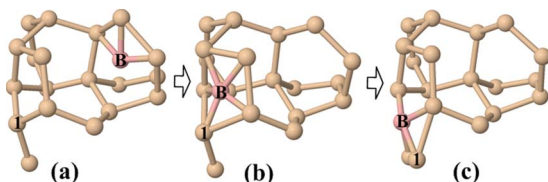


FIG. 2. (Color online) The diffusion of  $B_i$  through  $a$ -Si lattice.

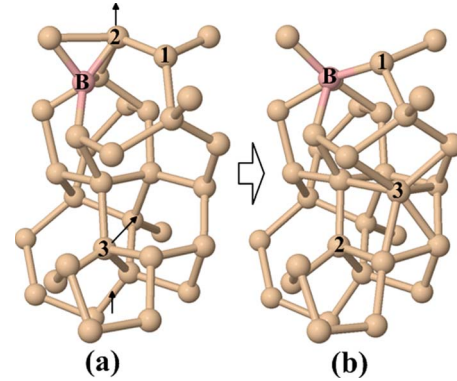


FIG. 3. (Color online) The mobility of kicked-out interstitials.  $B_i$  kicks out Si 2 and Si 2 kicks out Si 3. Due to periodic boundary conditions, Si 2 moves upward and injects from down side of Si 3.

of  $a$ -Si, or the formation of vacancies.<sup>6</sup> As shown in Figs. 2(a) and 2(b), B atom starts from a  $HB_i$  position and diffuses to a  $PB_i$  position, with a barrier of only 0.12 eV. The B finally kicks out a lattice Si and forms  $B_{\text{sub}}+I$ , as shown in Fig. 2(c). Combined with the previous knowledge that  $B_{\text{sub}}$  is well stabilized, we suggest  $B_i$  could be the major diffusion species in  $a$ -Si.

The  $B_i$ -based diffusion requires mobile Si interstitials to kick  $B_{\text{sub}}$  out to become  $B_i$ . Most of our MD simulations show that when  $B_i$  kicks in to be  $B_{\text{sub}}+I$ , the kicked-out  $I$  will move around and in many cases kick out another lattice Si. As shown in Fig. 3,  $B_i$  initially shares a lattice position with Si 2, then it kicks out Si 2, which diffuses for a relatively long distance and kicks out lattice Si 3. Given the 2 ps short simulation time, this scenario suggests the contribution to B diffusion from mobile interstitials over a longer time period. In a practical process, ion implantation will induce a large number of excess interstitials, which are unlikely for the  $a$ -Si network to accommodate and immobilize instantaneously. Since the relaxation of interstitials proceeds at the same pace as the reduction of DB,<sup>6</sup> while the latter is proved to be consistent with the transient feature of B fast diffusion in  $a$ -Si,<sup>5</sup> one cannot deny the possibility that the transient high interstitial concentration in  $a$ -Si will assist the B fast diffusion as well.

The stable  $B_{\text{sub}}$ , diffusing  $B_i$  and mobile interstitial in  $a$ -Si suggest an interstitial-based B diffusion mechanism, similar to the kick-out mechanism proposed earlier for B diffusion in  $c$ -Si.<sup>12</sup> As shown in Fig. 4, B tends to stay in the low energy  $B_{\text{sub}}$  position until an incoming interstitial knocks it out as  $B_i$ , which will jump between neighboring interstitial sites before falling back to  $B_{\text{sub}}$ . The activation energy for this mechanism can be estimated from the migration barrier  $E_m$  between two  $B_{\text{sub}}+I$  states, the interstitial formation energy,  $E_{fI}$ , and the binding energy,  $E_{\text{bind}}$ , of  $B_{\text{sub}}+I$  pair. The

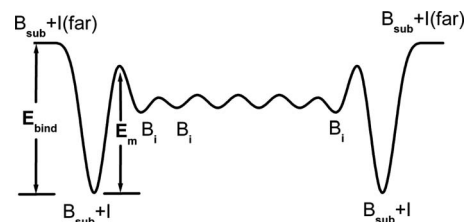


FIG. 4. Interstitial-based B diffusion mechanism in  $a$ -Si.

$E_{\text{act}}$  can be expressed as  $E_{\text{act}} = E_{\text{fl}} - E_{\text{bind}}(\text{B}_{\text{sub}} + I) + E_m(\text{B}_{\text{sub}})$ .

The interstitial formation energy is calculated by  $E_{\text{fl}} = E_{\text{total}}(a\text{-Si}) \times 65/64 - E_{\text{total}}(a\text{-Si} + I)$ , with an average over 35 samples including hexagonal, split, and randomly placed interstitials. For neutral interstitial in  $a\text{-Si}$ ,  $E_{\text{fl}}^0$  is calculated to be  $2.63 \pm 0.51$  eV. In the  $c\text{-Si}$  case, as a comparison,  $E_{\text{fl}}^0$  of hexagonal and split (110) interstitial is calculated to be 3.87 and 3.90 eV, respectively. The  $E_{\text{fl}}^0$  in  $a\text{-Si}$  is over 1.2 eV lower than that in  $c\text{-Si}$ , which is consistent with a previous study.<sup>7</sup> This lowering could be due to the bond rearrangement associated with interstitial integration in the  $a\text{-Si}$  lattice.<sup>7</sup> The formation energy of positively charged  $I^+$  is calculated to be  $E_{\text{fl}}^+ = 2.16 + E_F$  eV.

The  $E_{\text{bind}}$  of  $\text{B}_{\text{sub}} + I$  is assessed from the total energy difference between the configuration that  $\text{B}_{\text{sub}}$  and  $I$  are paired together, and the configuration that  $I$  is moved far apart from  $\text{B}_{\text{sub}}$  where the binding effect is minimized. The  $E_{\text{bind}}$  is calculated as  $0.60 \pm 0.35$  eV for neutral pairs ( $\text{B}_{\text{sub}} + I$ )<sup>0</sup>, and  $0.52 \pm 0.27$  eV for charged pairs ( $\text{B}_{\text{sub}} + I$ )<sup>+</sup>, each averaged over 22 samples.

To calculate the  $\text{B}_{\text{sub}}$ -to- $\text{B}_i$  barrier  $E_m$ , we construct NEBM pathways from  $\text{B}_{\text{sub}} + I$  to  $\text{B}_i$ , based on MD trajectories and local energy minimum sites. For neutral ( $\text{B}_{\text{sub}} + I$ )<sup>0</sup>,  $E_m$  is estimated to be  $0.70 \pm 0.35$  eV, while for ( $\text{B}_{\text{sub}} + I$ )<sup>+</sup> it is  $0.87 \pm 0.35$  eV, each averaged over 19 samples. Although there is no guarantee that the lowest barrier pathway can be found by this method, the accuracy of our results is enough for a semiquantitative estimation.

According to the above calculation,  $E_{\text{act}} = 2.73$  eV and  $(2.49 + E_F)$  eV for neutral and positively charged defect-based diffusion, respectively. Our calculated  $E_{\text{act}}$  agrees well with the experimentally reported activation energy range from 3.0 (Ref. 5) to 2.1 eV.<sup>2</sup> It can also be seen that the charged pair has a considerable diffusion contribution, especially in heavily  $p$ -doped cases, which is consistent with the experimentally reported concentration-dependent diffusion.<sup>1-3,5</sup> More importantly, the calculation shows that most of the

contribution to the  $E_{\text{act}}$  lowering is from the 1.2 eV lowering of  $E_{\text{fl}}$  compared to its value in  $c\text{-Si}$ . This suggests that the fast diffusion is mainly because interstitials have a larger concentration in  $a\text{-Si}$  than in  $c\text{-Si}$ , which should boost the interstitial-mediated  $B$  diffusion.

In summary, we propose an interstitial-based  $B$  diffusion mechanism in  $a\text{-Si}$ . In the  $a\text{-Si}$  lattice,  $B$  will preferentially stay in substitutional position as  $\text{B}_{\text{sub}}$ , while interstitial site  $\text{B}_i$  is the major diffusing species. The  $B$  fast diffusion can be explained by the energetically more favorable interstitial formation in  $a\text{-Si}$  than in  $c\text{-Si}$ . The interstitial-based mechanism is consistent with experiments for both activation energy and the transient and concentration-dependent features observed for  $B$  diffusion in  $a\text{-Si}$ .

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