

Triple-junction contribution to diffusion in nanocrystalline Si

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The influence of triple-junctions on experimental Ge diffusion profiles (850–1000 °C) in nanocrystalline Si is investigated using three-dimensional finite element simulations. We found that triple-junction diffusion is not negligible in nanocrystalline Si made of 40 nm wide grains. Ge triple-junction diffusion coefficient follows the Arrhenius law $5.72 \times 10^4 \exp(-3.24 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$. It is approximately 4.7×10^2 times higher than grain boundary diffusion coefficient, even though diffusion in triple-junction and in grain boundary exhibits similar activation energy. © 2010 American Institute of Physics. [doi:10.1063/1.3435476]

Nanocrystalline (nc) materials are of great interest for many industrial applications. For example, nanocrystalline Si (nc-Si) can be used in telecommunication applications¹ and in photodetector fabrication.² Hydrogenated nc-Si is a good candidate for solar cell fabrication:^{3–5} (i) it exhibits a low production cost, (ii) it can be used for all-Si tandem solar cell applications,³ since nc-Si band gap can be controlled from 1 to 3 eV by controlling nanograin size,⁵ (iii) quantum confinement and quantum effects can improve photocarrier transport and cell efficiency,⁵ and can allow multiple carrier generation.⁴ Nc-material production generally involves atomic diffusion during their processes. For example, applications such as photoluminescence, electroluminescence,⁶ and solar cells⁷ require Si nanocrystals or nc-Si layers to be doped with one or several impurities. Impurity diffusion studies in nc-materials, and in particular in nc-Si is thus very important, since mechanisms as self-purification,⁸ and structural properties of nc-materials can modify atomic transport properties, and complicate the doping processes. Triple-junctions (TJs), which correspond to the intersection of grain boundaries (GBs) in polycrystals, should play an important role upon atomic diffusion in nc-layers, as their density increases when grain size decreases. The properties of these one-dimensional defects are still not very well known. Theoretical considerations agree that TJs should be treated as independent defects, different than interfaces and GBs.⁹ Recent molecular dynamic (MD) simulations by Frolov and Mishin¹⁰ showed that in Cu TJs exhibit a higher positive excess energy than GBs. Other MD simulations¹¹ showed that in Si, TJs are different defects than GBs with positive excess energy, and are source of residual stress. Positron experiments on nc-Fe (Ref. 12) confirmed that TJs and GBs are different: free volumes at interfaces like GBs correspond to single vacancies, while interface intersections as TJs exhibit microvoids that correspond to vacancy agglomeration. The influence of TJs on impurity diffusion in nc-materials depends upon impurity mobility in TJs and TJs volume proportion, i.e., the TJ contribution is not negligible if $f_{ij}D_{ij} \geq f_{gb}D_{gb} \geq f_gD_g$, with f_{ij} , f_{gb} , and f_g the respective volume fraction of TJs, GBs, and grains, and D_{ij} , D_{gb} , and D_g the diffusion coefficients in TJs, GBs, and grains, respectively.

TJ effect is expected to be significant at low temperature, at which $D_{ij} \gg D_{gb}$ and D_g , and for grain size lower than 10 nm, since in this case $f_g \leq 0.8$, $f_{gb} \geq 0.2$ and $f_{ij} \geq 0.02$.¹³ However, Chen and Schuh¹⁴ suggested that TJs can influence diffusion in nc-materials made of 100 nm wide grains, for temperatures lower than $0.8 \times T_m$, with T_m the matrix melting temperature. Experimentally, nc-materials exhibit diffusivities of several orders of magnitude larger than in microcrystalline (mc) materials. However, due to the difficulty to separate the TJ contribution from the GB contribution in diffusion profiles, it is not clear if these results can be attributed to a higher diffusivity in nano-GBs compared to micro-GBs, or to a higher diffusivity in TJs compared to GBs. Diffusion coefficient measurements performed in polycrystalline materials using models that consider TJs are quite rare,¹⁵ the Fisher model¹⁶ being generally used to study diffusion in polycrystals. For example, Cu GB diffusion coefficient measured at $0.23–0.27 \times T_m$ in nc-Ni (grain sizes 100–300 nm) was found to be 10^5 times faster than in mc-Ni.¹⁷ Zn diffusion in polycrystalline Al was clearly shown to be faster in TJs than in GBs,¹⁸ with $D_{ij}/D_{gb} \sim 10^3$ at $0.6 \times T_m$. Furthermore, Chen and Schuh¹⁹ showed that using a diffusion model taking into account TJs, experimental studies on metals performed at $\sim 0.2–0.3 \times T_m$ give $10^3 \leq D_{ij}/D_{gb} \leq 10^8$.

Despite the high potential of nc-semiconductors for industrial applications, studies treating of TJ influence upon atomic transport in these materials are rare. In a previous work,²⁰ we measured and compared Ge diffusivity in grains (lattice diffusion) and GBs in microcrystalline and nanocrystalline Si (40 nm wide grains) at 850–1000 °C, using Fisher's model and two-dimensional (2D model) finite element simulations (FES). Ge diffusion in Si is ideal to study diffusion in nc-semiconductors since: (i) Si(Ge) layers can be produced with microelectronics purity level and ideal density (no porosity), (ii) nc-Si layers are produced without compaction or severe plastic deformations that can add complexity, (iii) Ge is a fully soluble substitutional impurity in Si, (iv) Ge lattice diffusion uses the same vacancy mechanism in our experimental conditions, and (v) Ge segregation in Si GBs has not been observed. The Ge diffusion coefficients in nc-Si (nc- D_g and nc- D_{gb}) were found about one order of magnitude faster than in mc-Si (mc- D_g and mc- D_{gb}). The activation energy (E_a) was found about 1 eV lower in nanograins (nc- E_g) than in micrograins (mc- E_g), while similar E_a was

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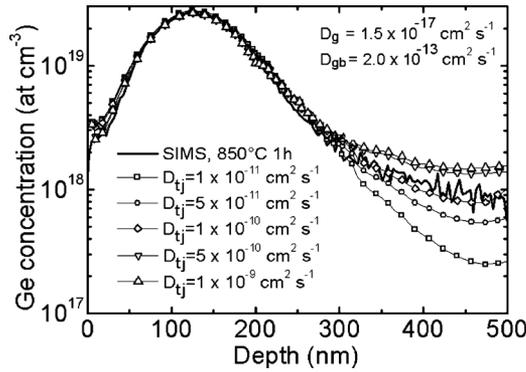


FIG. 1. SIMS profile after annealing at 850 °C for 1 h, and simulated profiles with $D_g = 1.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$, $D_{gb} = 2.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, and $10^{-11} \leq D_{tj} \leq 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

found in nano-(nc- E_{gb}) and micro-GBs (mc- E_{gb}).

The present study investigates TJ influence on Ge diffusion in nc-Si in the $0.67\text{--}0.76 \times T_m$ temperature range. We used the same experimental Ge diffusion profiles as presented in Ref. 20. The fitting process was the same as described in Ref. 20, a cubic geometry similar to Fisher's model was used to extract diffusion coefficients, except that FES using a three-dimensional (3D) model including TJs was employed. In this geometry, the three diffusion coefficients D_g , D_{gb} , and D_{tj} can be extracted but not independently.^{20,21} Furthermore, the contribution fractions of grains, GBs and TJs are different in the 2D and 3D geometries, with $f_g = 0.98765$, $f_{gb} = 0.01235$, and $f_{tj} = 0.0$ for the 2D model, and $f_g = 0.97546$, $f_{gb} = 0.02439$, and $f_{tj} = 0.00015$ for the 3D model. Nevertheless, for same D_g and D_{gb} (with $D_{gb} = D_{tj}$ for the 3D model) the simulated profiles of the 2D and 3D models were found to be very similar. For 40 nm grains, differences less than 20% were found in diffusion coefficients between the 2D and 3D models. Figure 1 presents the Ge experimental secondary ion mass spectrometry (SIMS) profile measured in the nc-Si layer after annealing at 850 °C for one hour, as well as simulated profiles obtained for the same annealing conditions with same $D_g = 1.5 \times 10^{-17}$ and $D_{gb} = 2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, but for various D_{tj} values, from 10^{-11} to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$. D_g and D_{gb} correspond to the nanograin diffusion coefficient, and to the micro-GB diffusion coefficient measured at this temperature in Ref. 20, respectively. The variation in D_{tj} corresponds to a ratio D_{tj}/D_{gb} comprise between 5×10^1 and 5×10^3 , which is realistic considering previous works.^{18,19} This figure clearly shows that Ge diffusivity in TJs cannot be neglected in nc-Si made of 40 nm wide grains, since the final 1D Ge profile is highly dependent upon the value of D_{tj} . Furthermore, the Ge experimental profile can be fitted using the same GB diffusion coefficient as measured in mc-Si and considering a TJ diffusion coefficient of about $1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. As we showed in Ref. 20, D_g and D_{gb} can be determined simultaneously from FES if the value of D_{tj} is known. In order to understand the effect of TJ diffusivity on the coefficients that we measured in nanograins and nano-GBs using the 2D Fisher geometry, we fixed the value of D_{tj} to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, and extracted the values of D_g and D_{gb} by fitting the experimental Ge diffusion profiles.²⁰ $D_{tj} = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ is at least two orders of magnitude higher than the GB diffusion coefficient we measured in mc-Si,²⁰ while it is at least three orders of magnitude lower than Si

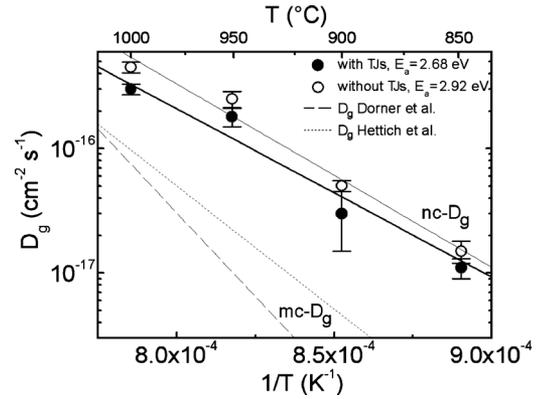


FIG. 2. Nc- D_g from 2D simulations without TJs (open symbols) and from 3D simulations with TJs (solid symbols) with $D_{tj} = 1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Ge lattice diffusion coefficients from Dornier *et al.* (dashed line) and Hettich *et al.* (dotted line) are also presented.

surface self-diffusion²² in our temperature range. Figure 2 presents the temperature dependence of the diffusion coefficients in nanograins (nc- D_g) measured using the 2D geometry without TJs (open symbols) (Ref. 20) and using the 3D geometry with TJs (solid symbols), as well as the diffusion coefficients measured in monocrystalline Si (mc- D_g) by Dornier *et al.*²³ (dashed line) and Hettich *et al.*²⁴ (dotted line). The coefficients measured using the two different geometries are very similar, with similar activation energies. This is due to the very small surface area of grain/TJ interfaces, which leads to negligible direct atom exchanges between grains and TJs. The same conclusion as made in Ref. 20 can be given with the 3D geometry: nc- D_g is one order of magnitude higher than mc- D_g , and nc- E_g is at least 1 eV smaller than mc- E_g . Figure 3 presents the temperature dependence of nc- D_{gb} measured using the two different geometries without (open symbols) and with TJs (solid symbols), as well as mc- D_{gb} using the lattice diffusion coefficients of Dornier *et al.* (dotted line) or Hettich *et al.* (dashed line). The activation energies in nano-GBs measured using the 2D (nc- $E_{gb} \sim 3.54 \text{ eV}$) and the 3D (nc- $E_{gb} \sim 3.80 \text{ eV}$) geometries are comparable. However, the 3D nc- D_{gb} is found about one order of magnitude lower than the 2D nc- D_{gb} . It can be noticed that considering a constant $D_{tj} = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, the 3D nc- D_{gb} is found to be similar to the mc- D_{gb} (using D_g of

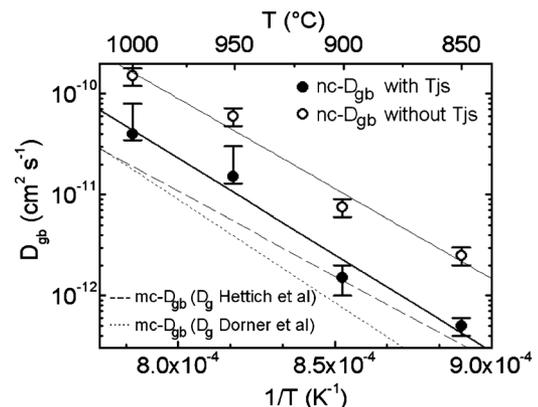


FIG. 3. Nc- D_{gb} from 2D simulations without TJs (open symbols) and from 3D simulations with TJs (solid symbols) with $D_{tj} = 1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Ge GB diffusion coefficients measured in mc-Si using the Ge lattice diffusion coefficient either from Dornier *et al.* (dotted line) or Hettich *et al.* (dashed line) are also presented.

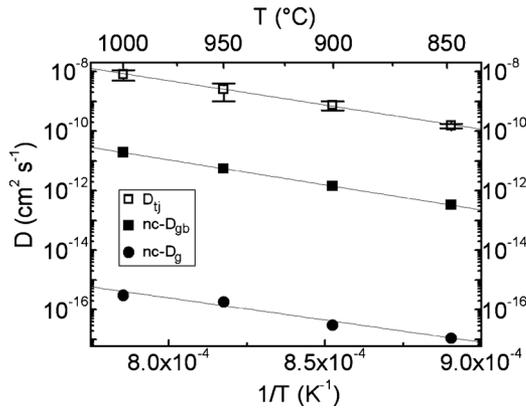


FIG. 4. D_{ij} (open squares) and $nc-D_g$ (solid circles) measured in nc-Si considering that $nc-D_{gb}$ is the same as $mc-D_{gb}$ (solid squares).

Hettich *et al.*), for the two lower temperatures (900 and 850 °C). This observation suggests that TJ diffusion coefficients at 1000 and 950 °C are higher than 10^{-9} $\text{cm}^2 \text{s}^{-1}$. Considering an average TJ effect (constant D_{ij}) upon Ge diffusion in nc-Si, nano-GB diffusion coefficients are found to be close to micro-GB diffusion coefficients. Combining the results obtained on Ge diffusion in nc-Si without taking into account TJs (Ref. 20) and considering TJs, it can be concluded that (i) $nc-D_g$ is faster than $mc-D_g$: the nanosize effect increases the vacancy concentration in nanograins compared to bulk, due to the influence of the grain surfaces²⁰ (Beckman and Chelikowsky²⁵ have shown that reducing Si nanocrystal size can decrease the formation and the migration energies of Si vacancies), (ii) $nc-D_{gb}$ and $mc-D_{gb}$ are the same: the nanosize effect does not drastically change the nature of GBs,²⁰ in agreement with the work of Caro and Van Swygenhoven²⁶ showing that nano-GBs and micro-GBs exhibit similar structures, size, energies and disorder, and (iii) TJs have an effect on Ge diffusion even for 40 nm wide Si grains. Consequently, the 2D model cannot be used to measure grain boundary diffusion in nanocrystalline layers. The Ge TJ diffusivity in nc-Si can be measured in our experiments using 3D FES, considering D_g to be the same as the $nc-D_g$ measured in Ref. 20, and D_{gb} to be the same as the $mc-D_{gb}$ measured in Ref. 20. Figure 4 presents the Ge TJ diffusion coefficients measured in nc-Si (open symbols), as well as the $nc-D_g$ (solid circles) and the $mc-D_{gb}$ (solid squares) from Ref. 20. The Ge TJ diffusion coefficient is found to be $D_{ij} = 5.72 \times 10^4 \exp(-3.24 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$, with an average $D_{ij}/D_{gb} \sim 4.7 \times 10^2$. D_{ij} and D_{gb} are found to have similar activation energy, meaning that the difference between the two coefficients is mainly due to different Arrhenius prefactors (D_0). This is in agreement with experimental¹² and theoretical¹⁰ works showing that the principal difference between GBs and TJs is a higher disorder degree in TJs. D_0 contains, among several factors, the entropic component that is proportional to disorder, a higher D_0 corresponding to a higher degree of disorder. Similar to our observations, Frolov and Mishin¹⁰ predicted a faster Cu self-diffusivity in TJs than in GBs mainly due to a larger TJ Arrhenius prefactor than the

GB one ($TJ-E_a = 0.47$ eV and $\Sigma 5GB-E_a = 0.48$ eV). However, Frolov and Mishin¹⁰ predicted a TJ D_0 only two times higher than the GB D_0 . This difference with experimental results may be due to an entropy increase related to the additional chemical disorder involved with impurity diffusion in experiments, instead of self-diffusion in simulations. In addition, Belova and Murch²⁷ proposed that the high diffusion rate observed experimentally can be due to multiple-atom-jump mechanisms.

In conclusion, Ge diffusion in nc-Si has been investigated using 3D FES in the $0.67-0.76 \times T_m$ temperature range. TJ diffusion is not negligible for Ge diffusion in nc-Si made of 40 nm wide grains. Consequently, 2D models cannot be used to extract grain boundary diffusion in nanocrystalline layers. Ge lattice diffusion is found one order of magnitude faster in Si nanograins compared to monocrystalline Si. Ge diffusion is identical in nano-GBs and in micro-GBs, while Ge diffusion is faster in TJs ($\times 4.7 \times 10^2$) than in GBs. This work shows that Ge enhanced diffusion in nc-Si results from two contributions: (i) faster lattice diffusion in nanograins and (ii) fast diffusion in TJs.

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