Comment on "Contributions of vacancies and self-interstitials to self-diffusion in silicon under thermal equilibrium and nonequilibrium conditions"

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Our main comment is that the data at low temperatures of Kube *et al*. [Phys. Rev. B **88**, 085206 (2013)] and those of Shimizu *et al*. [Phys. Rev. Lett. **98**, 095901 (2007)] may not have been due to intrinsic vacancies but rather to extrinsic vacancies generated at carbon and/or vacancy clusters, depending on the specimens used.

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Experimental determination of the activation energy (E_D^V) of vacancy-mediated self-diffusion in silicon crystals is a long-standing issue. Kube *et al*. [1] studied self-diffusion of the multilayer (ML) structure of isotope Si (20 bilayers of ^{28}Si/^{29}Si) and of a sandwiched (SW) structure (^{nat}Si/^{28}Si/^{nat}Si) at low temperatures (650–950 °C) with measurements by secondary ion mass spectroscopy (SIMS) and neutron reflectivity (NR). The former and the latter specimens were grown by molecular-beam epitaxy (MBE) and by the chemical vapor deposition method (CVD), respectively. Kube *et al*. [1] analyzed their data of the SW structure together with those of Bracht *et al*. [2] at high temperatures (855–1378 °C) and reported E_D^V as well as E_D^I (the activation energy of interstitial-mediated self-diffusion) to be 3.52 and 4.92 eV, respectively. These values were in good agreement with those (3.6 and 4.95 eV) reported by Shimizu *et al*. [3] from measurements of diffusion with Raman spectroscopy in the ML structure (20 bilayers of ^{28}Si/^{30}Si). Kube *et al*. [1] considered these values to be those of an intrinsic crystal since the results of the two groups [1,3] agreed well. To solve the inconsistency that E_D^V was smaller than that (4.08 eV) of Sb diffusion [4], Kube *et al*. [1] introduced the temperature dependence of the thermodynamic properties of vacancies, such as the energies of formation and migration, and entropies of formation and migration, which were first proposed by Seeger *et al*. [5].

Our Comment is on the preferential sites of vacancy formation, i.e., the sites where the formation energy is smaller than that in a perfect crystal. Carbon in the specimens of SW and ML and vacancy clusters in the ML structure are such sites. The carbon concentrations in ML and SW are 3×10^{18} and 5×10^{17} cm^{-3}, respectively [1]. Kube *et al*. [1] assumed that only electrically active impurities have an effect on the charged vacancy formation but offered no explanation on the neutral vacancy concentration which was responsible for the self-diffusion in their specimen. By a quenching experiment, however, we determined the vacancy formation energy in the carbon-doped specimen to be 3.2 eV [6,7] (determined to be 3.08 ± 0.15 eV after reanalysis of data obtained from quenching between 1200 and 1360 °C), much smaller than 3.85 eV [8,9] (determined to be 3.85 ± 0.15 eV after reanalysis of data obtained from quenching between 1200 and 1360 °C) by our quenching experiment using a high-purity crystal. Nelson *et al*. [10] calculated the binding energies between various impurity atoms and a vacancy. According to them, the binding energy between the carbon and a vacancy was 0.11 eV, and hence the vacancy formation energy was 3.58 eV since the formation energy in a perfect crystal was estimated to be 3.69 eV by their calculation. Other theoretical estimates have shown that an electrically neutral impurity, such as Sn in Si, has a large binding energy with a vacancy [11]. On the other hand, many vacancy clusters have been detected by positron annihilation studies in MBE-grown structures [12]. The binding energy between the vacancy clusters and a vacancy was estimated to be about 3.2 eV [13]. Hence, the vacancy formation energy from vacancy clusters is 3.2 eV. These results suggest that the data obtained at low temperatures may have been greatly influenced by carbon atoms, not by carbon precipitates, and by vacancy clusters. Hence, the interpretation that the activation energy of vacancy-mediated diffusion was intrinsic would seem to be doubtful.

An abnormally small preexponential factor of vacancy-mediated diffusion seems to be easily explained by the above discussion since the concentration of carbon and/or the density of vacancy clusters are probably involved in the preexponential factor. If we assume that the simultaneous analyses of diffusion data made by Kube *et al*. [1] and by Shimizu *et al*. [3] are appropriate, the difference in the preexponential factors between 0.0011 of Kube *et al*. [1] and 0.0023 of Shimizu *et al*. [3] can be attributed to the difference in the density of preferential vacancy sites.

Incidentally, if the above view that the low-temperature data were influenced by carbon and/or vacancy clusters is correct, there is no reason to analyze the data at high temperatures and low temperatures simultaneously. Plotting numerical data of Kube *et al*. [1] and those of Bracht *et al*. [2] (self-interstitial) and Shimizu *et al*. [3] in larger magnification than Fig. 4 in Ref. [1], we noticed that the relations between log D and $1/T$ of all data were approximately linear. We attempt to analyze those data, even though it may be beyond the readers' situation. Figure 1 shows an example. Solid circles correspond to the data of SW. Probably the size of circles should be larger than this plot if we take the experimental error into consideration. The solid line and the broken line correspond to the fitting lines due to the least-squares fit of the data of SW and Eq. (7) in Ref. [1], respectively. In Fig. 2, data of SW and Shimizu *et al*. [3] are plotted together with the least-squares fitting lines of the solid and broken lines, respectively. Both data agree well. However, as shown by the solid and broken lines, activation energies are slightly different. It is not easy to understand relations among various data from Fig. 4 in Ref. [1]. Hence, in Fig. 3 we show the fitting lines without data points of various data. Solid and open circles correspond to the data at the highest

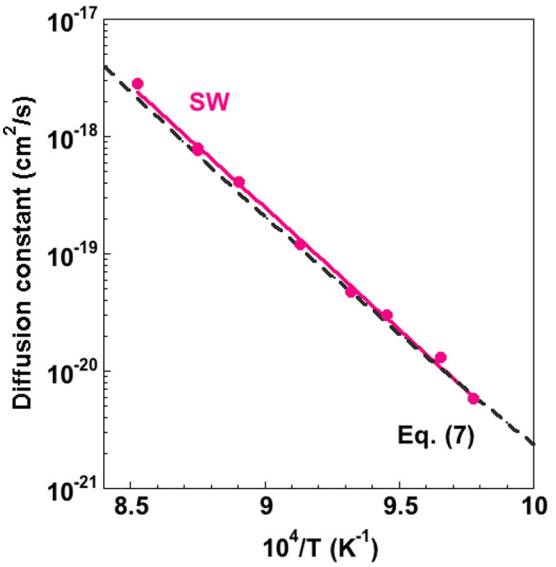

FIG. 1. (Color online) Data of SW (solid circles) in Ref. [1] and the least-squares fitting line (solid line). The broken line is calculated from Eq. (7) in Ref. [1].

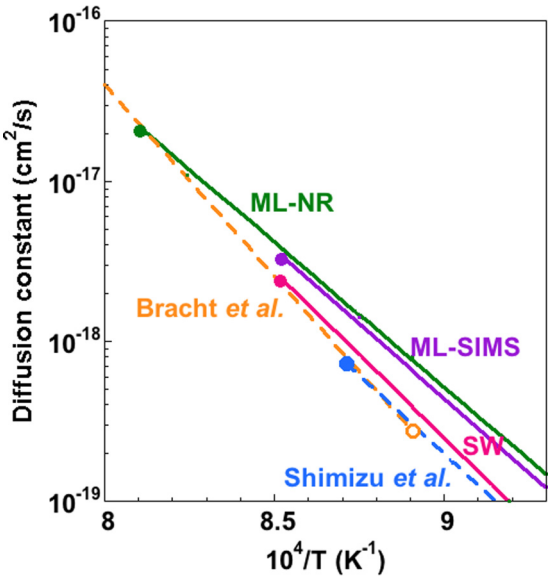

FIG. 3. (Color online) Results of the least-squares fit of various data sets. The data points were omitted. The solid and the open circles correspond to the highest and the lowest temperatures, respectively, of the measurements.

and the lowest temperatures, respectively, in each piece of data. Roughly, the four lines at low temperatures seem to be almost parallel to each other. We determined the activation energy and the preexponential factor for each piece of data by the least-squares fit. The results of the analyses are shown in Table I. The activation energy and entropy are larger than those determined from the simultaneous analysis combining both data at high temperatures and those at low temperatures. The entropy term is very sensitive to the activation energy since it is determined from the extrapolation of data between about 8 and 10 of $10^4/T$ to 0. From Table I, the vacancy formation energy is estimated to be between 3.00 and 3.68 eV since the migration energy of the vacancy was estimated to be about 0.45 eV [14]. The numerical values are in fairly good agreement with the vacancy formation energy associated with carbon 3.1 eV and the binding energy between vacancy clusters and a vacancy 3.2 eV.

In conclusion, the data at low temperatures of Ref. [1] and those of Shimizu *et al.* [3] are possibly not intrinsic but extrinsic, i.e., being related to carbon and vacancy clusters. Hence,

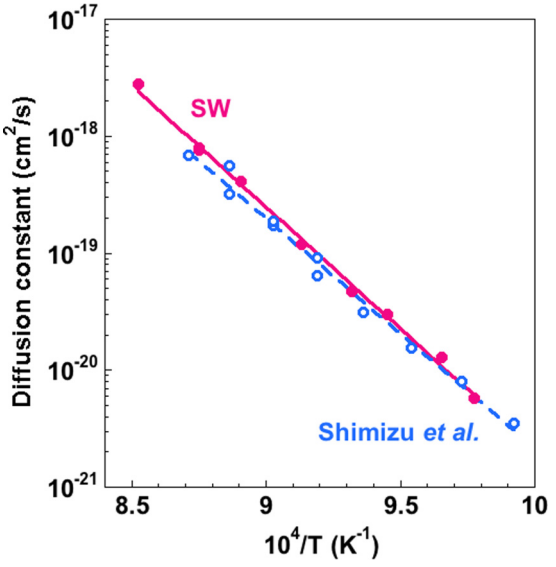

FIG. 2. (Color online) Data of SW (solid circles) in Ref. [1] and those (open circles) of Shimizu *et al.* [3]. Solid and broken lines are the fitting lines to those data of SW and Shimizu *et al.* [3], respectively, due to the least-squares fit.

TABLE I. Results of E_D^V and the preexponential factor determined by the least-squares fit to the low-temperature data, together with preferential site and concentration for vacancy formation. The abbreviations are methods of specimen preparation and measurements; Raman: Raman spectroscopy. The unit of the preexponential factor is the Boltzmann constant (k_B).

Specimen growth method	Measurement method	E_D^V (eV)	Preexponential factor (k_B)	Preferential site concentration (cm^{-3})
SW CVD	SIMS	4.13	1.282	5×10^{17}
ML MBE	SIMS	3.45	0.002	Vacancy cluster 3×10^{18}
ML MBE	NR	3.61	0.012	Vacancy cluster 3×10^{18}
ML MBE	Raman	3.90	0.096	Vacancy cluster –[a]

[a]Specimens of Shimizu *et al.* [3] were of high purity. The status of silicon technology in 2007, however, suggested that their specimens contained about 1×10^{16} cm^{-3} of carbon.

the temperature dependence of thermodynamic properties of the vacancy seems unnecessary to explain the experimental results.

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