Reply to “Comment on ‘Contributions of vacancies and self-interstitials to self-diffusion in silicon under thermal equilibrium and nonequilibrium conditions’”

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Suezawa *et al.* [*Phys. Rev. B* **90**, 117201 (2014)] claim in their Comment that the data reported by Shimizu *et al.* [*Phys. Rev. Lett.* **98**, 095901 (2007)] and Kube *et al.* [*Phys. Rev. B* **88**, 085206 (2013)] on silicon self-diffusion for temperatures between 900 and 735 °C are affected by carbon and vacancy clusters and, accordingly, do not reflect self-diffusion under thermal equilibrium conditions. We demonstrate in our Reply that an impact of carbon on self-diffusion can definitely be excluded. In addition it is rather unlikely that the self-diffusion data reported by Shimizu *et al.* [*Phys. Rev. Lett.* **98**, 095901 (2007)] and Kube *et al.* [*Phys. Rev. B* **88**, 085206 (2013)] are affected by the dissolution of vacancy clusters since strong differences exist not only in the preparation of the samples used for the experiments, but also in the time of diffusion. Finally, the vacancy formation enthalpy deduced by Suezawa *et al.* [*J. Appl. Phys.* **110**, 083531 (2011)] from quenching experiments is consistent with the value obtained from the temperature dependence of the vacancy formation enthalpy reported by Kube *et al.* [*Phys. Rev. B* **88**, 085206 (2013)]. Overall we conclude that the quenching experiments of Suezawa *et al.* [*J. Appl. Phys.* **110**, 083531 (2011)] cannot disprove the interpretation of the low-temperature self-diffusion data reported by Shimizu *et al.* [*Phys. Rev. Lett.* **98**, 095901 (2007)] and Kube *et al.* [*Phys. Rev. B* **88**, 085206 (2013)].

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Before we reply to the Comment of Suezawa *et al.* [1] in detail it is noted that the temperature dependence of self-diffusion reported by Shimizu *et al.* [2] and Kube *et al.* [3] for equilibrium conditions are accurately described with temperature-dependent thermodynamic properties of vacancies (*V*) and temperature-independent properties of self-interstitials (*I*). The activation enthalpy of self-diffusion via *V* and *I* are fully consistent to *V*- and *I*-mediated dopant diffusion in Si. It is also noteworthy that the temperature dependence of the formation enthalpy of *V* yields a value of 3.76 eV for 1300 °C that is in accurate agreement with the vacancy formation enthalpy of 3.85 eV at high temperatures determined by Suezawa *et al.* [4] for high-purity Si crystals. This shows that results of the quenching experiments of Suezawa *et al.* [4] also support the *V*-mediated self-diffusion proposed by Kube *et al.* [3] rather than to provide clear evidence on extrinsically enhanced self-diffusion by *V* generated at carbon and/or *V* clusters.

In the following we will discuss in more detail the Comment of Suezawa *et al.* [1] on the impact of *V* generated at carbon on self-diffusion. The Si isotope structures used by Shimizu *et al.* [2] and Kube *et al.* [3] for self-diffusion were grown by molecular-beam epitaxy (MBE) and chemical vapor deposition (CVD), respectively. The carbon concentration of the MBE-grown samples is below the detection limit of secondary ion mass spectrometry (SIMS) and is estimated to be 10^{16} cm^{-3} . The carbon content of the CVD-grown samples was determined with SIMS to be $5 \times 10^{17} \text{ cm}^{-3}$. Despite these different carbon contents of the MBE and CVD samples, both sets reveal consistent data for self-diffusion at low temperatures [3]. In fact, we can state that *V* generated

at carbon is not expected to affect self-diffusion. Certainly, the formation of *V* at carbon is reduced by the binding energy between carbon and *V*. But in order that vacancies formed at carbon can mediate self-diffusion the carbon-*V* pairs must dissociate, i.e., the binding energy must be overcome. Accordingly, the total energy to supply *V* for self-diffusion is equal to its formation enthalpy in high-purity Si. This shows that *V*'s generated at carbon are not expected to enhance self-diffusion except in the case where a huge carbon concentration exists. In this hypothetical case the carbon-*V* pairs are considered as an infinite source of *V*, whose dissociation supplies *V* for self-diffusion. Then the apparent formation enthalpy of *V* would equal the dissociation energy of the carbon-*V* pair. Since the binding energy for this pair is with 0.11 eV [5] very low, the activation enthalpy of *V*-mediated self-diffusion should be lower than 1 eV. The experimental data on self-diffusion reported by Shimizu *et al.* [2] and Kube *et al.* [3] certainly can exclude such *V*-mediated self-diffusion via *V* injection from carbon-*V* pairs.

On the other hand *V* clusters might serve as efficient sources of *V*. This has been considered by Kube *et al.* [3] to describe the self-diffusion in their MBE-grown structures, which is clearly enhanced compared to self-diffusion in the CVD samples. Modeling of self-diffusion in the MBE samples reveals a binding energy of 3.2 eV for the *V* clusters that is in accurate agreement with values reported in the literature [6,7]. Accordingly, we do not question a *V* formation by *V* clusters but consider it highly unlikely that the samples of Kube *et al.* [3] grown by CVD at 800 °C and the samples of Shimizu *et al.* [2] grown by MBE at 650 °C possess *V* clusters of the

same type and in the same concentration. Furthermore, these two sets of samples are different not only with regard to their preparation history, but also in view of the diffusion length realized in the experiment. The diffusion length $(2D_{\text{Si}}t)^{0.5}$ (where D_{Si} is the Si self-diffusion coefficient and t is the diffusion time) established in the experiments of Shimizu *et al.* [2] is about a factor of 10 lower than the diffusion length realized by Kube *et al.* [3] with the CVD-grown samples. In fact, the broadening of the Si isotope structure of the CVD samples for temperatures below 850 °C is similar in magnitude to the broadening established in former experiments with the same as-grown samples for temperatures exceeding 850 °C [8]. The pronounced broadening at the lower temperatures is achieved by extending the time for self-diffusion to several months. In the case where the self-diffusion in the CVD-grown samples at low temperatures is due to V 's released from grown-in V clusters this should also hold for the experiments at higher temperatures that show a similar magnitude of self-atom mixing. However at these temperatures and times V -related defect clusters are already fully dissolved as indicated by the absence of any transient-enhanced self-diffusion in recent and former self-diffusion studies with the CVD samples. The differences in the growth conditions of the samples used by Shimizu *et al.* [2] and Kube *et al.* [3] and the differences in the annealing conditions make it highly unlikely that the two sample sets reveal equal self-diffusion data for low temperatures that are affected by the dissolution of V clusters. This led us to conclude that the results reported by Shimizu *et al.* [2] and Kube *et al.* [3] for Si self-diffusion at low temperatures reflect data for thermal equilibrium conditions.

Finally, we would like to reply to the analysis of Suezawa *et al.* [1] of the self-diffusion data at low temperatures. Showing only self-diffusion data from a limited temperature range will certainly reveal a single Arrhenius-type temperature dependence since all self-diffusion data of Kube *et al.* [3] and Shimizu *et al.* [2] only reveal a small curvature in logarithmic representation. This treatment of Suezawa *et al.* [1] is misleading because it neglects that besides V also I contributes to self-diffusion. Neglecting the contribution of I suggests a higher activation enthalpy for V -mediated self-diffusion than in the case where both contributions are considered. Suezawa *et al.* [1] argue that the activation enthalpy for V -mediated self-diffusion yields a V -formation enthalpy that is in fairly good agreement with the V formation and binding energy associated with carbon and V clusters, respectively. This apparent agreement is not sufficiently significant to verify an impact of carbon and/or V clusters on self-diffusion at low temperatures. Contrariwise, the good agreement of the V -formation enthalpy of 3.85 eV determined from the quenching experiments with high-purity Si crystals [4] and of 3.76 eV for 1300 °C [3] obtained from the temperature dependence of the V -formation enthalpy indicates that the quenching study can even support the temperature-dependent thermodynamic properties of V proposed by Kube *et al.* [3].

In conclusion, the temperature dependence of the thermodynamic properties of V in Si proposed by Kube *et al.* [3], which explains the temperature dependence of Si self-diffusion, can be neither disproved nor proved by the quenching experiments of Suezawa *et al.* [4].

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