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Response to "Comment on 'Structural, electronic, and optical properties of the C-C complex in bulk silicon from first principles" [J. Appl. Phys. 123, 161421 (2018)]"

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Abstract : In this Reply, we discuss the relative stability of different forms of C_iC_s complexes. Based on the extended sections of IR absorption spectra reported by Lavrov [Lavrov2018] in his Comment, we identify that the *C form* is stabilized transiently in FZ-silicon during and just after electron irradiation. For longer time at room temperature, the *C form* disappears at the expense of the *B form*. Nonetheless, the *C form*, was found to be stable up to 280°C in Cz-silicon after neutron irradiation [Sgourou2013]. We attribute this apparent discrepancy to a vacancy-induced C_iC_s dissolution mechanism that drives the electron irradiated sample in a non-equilibrium state that differs from the equilibrium state predicted by DFT calculations [Timerkaeva2018]. In the neutron irradiation experiment, the generated vacancies are trapped by oxygen interstitial allowing the thermodynamics equilibrium to be preserved.

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In his Comment to our paper [Timerkaeva2018], Lavrov reports broader range of frequencies [Lavrov2018] than in his seminal experiments [Lavrov1999]. Our hypothesis [Timmerkaeva2018] that the presence of *C form* complexes could be hidden by the *B form* is now clearly discarded for the long time room temperature (RT) annealed sample (95 min). Indeed no line appears in the 1100-1200 cm^{-1} range for the same annealing time as those presented in the initially published spectra (figure 1 in [Lavrov1999]).

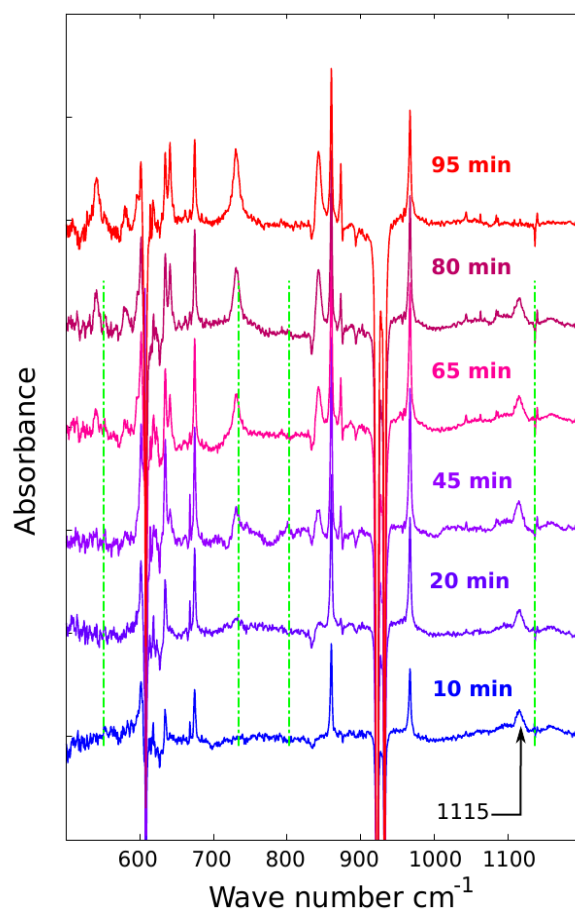


Figure 1: Six first FTIR spectra from [Lavrov2018] together with the four expected LVM frequencies range as predicted by DFT [Timerkaeva2018] for the *C form* of the C_iC_s complex (green dotted lines).

Interestingly, the new data also include five spectra (figure 1) with shorter RT annealing time with respect to the initially published data set. A striking feature that appears in these spectra, is the existence of a broad and small line at 1115 cm^{-1} that disappears after 80 minutes. Although this new line could be an artifact coming from a non-ideal subtraction, the fact that it appears only for short annealing times is puzzling and denotes the existence of a transient complex. Similarly, before 60 minutes, the 6 lines denoting the *B form* [Lavrov1999] are absent or weak, meaning that the *B form* is not the one created right after irradiation but the result of a transformation at RT. We have added on figure 1, the calculated Localized Vibrational Modes (LVM) frequencies [Timerkaeva2018] for the *C form* of the complex, respectively 549, 735, 801 and 1135 cm^{-1} . It is worth noticing that the two first lines of the *C form* overlap with three lines of the *B form*, the main feature for the *C form* being the $>1100 \text{ cm}^{-1}$ line.

We interpret the presence of the 1115 cm^{-1} experimental line as a strong clue for the presence of the *C form* just after the electron irradiation and in the first hour of the annealing. After the first hour, the *B form* starts to appear at the expense of the *C form* that completely disappears after one hour and a half. In other words, the *C form* would be the form stabilized in the course of the irradiation. However it seems to be unstable as it quickly dissolves at room temperature in the experiment of Lavrov [Lavrov2018]. This piece of evidence is in the line with the analysis we have made for neutron irradiated silicon samples where a C_iC_s complex was also detected [Sgourou2013] and identified as the *C form* on the basis of its dissociation kinetics [Brenet2015] at intermediate temperature.

Such a dissociation kinetics was also presented by Lavrov *et al.* [Lavrov1999] and can be used to confirm that the observed C_iC_s in the two experiments are complexes of different forms. Indeed, we have already reported [Brenet2015] that a difference of more than 100°C exists for the dissociation temperature of the 549 cm^{-1} line, with the used annealing ramp ($10^\circ\text{C}/20\text{ min}$) [Sgourou2013]. The experimental on-set for dissociation in Ref. [Sgourou2013], matches the calculated one for the *C form*. Now, we can repeat the same Kinetic Mass Action Law (KMAL) simulations for the annealing ramp used by Lavrov *et al.* ($20^\circ\text{C}/30\text{ min}$), see Figure 2. The experimental on-set for dissociation is $\sim 210^\circ\text{C}$ (for the 540 and 543 cm^{-1} lines, figure 3 in Ref. [Lavrov1999]) while the simulated temperatures are 170°C and 280°C for the *B form* and the *C form*, respectively. This result is in the line with the presence of the *B form* in Lavrov samples and confirm the relevance of this method to distinguish between the two forms.

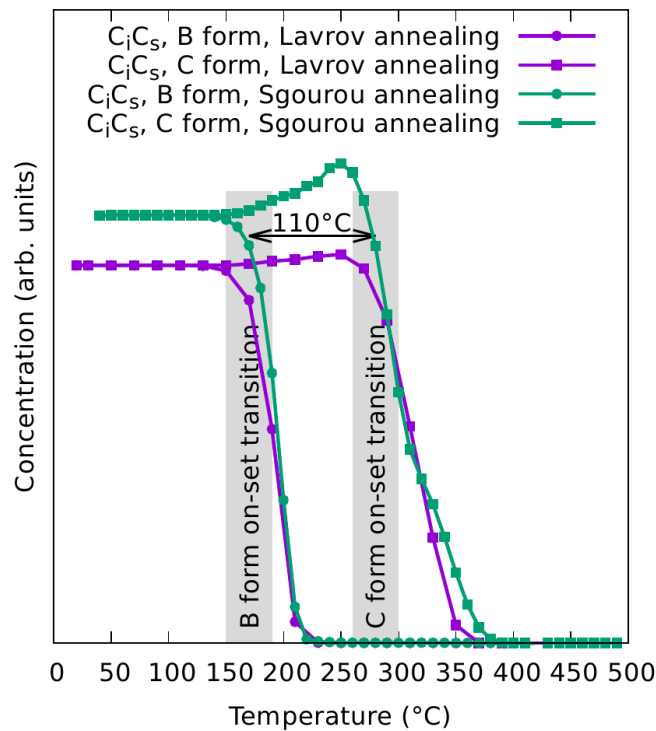


Figure 2: KMAL simulations in the case of B or C form (circle and square resp.) using the same conditions as in Ref. [Brenet2015] and the two annealing sequences (see text) in both Lavrov [Lavrov1999] and Sgourou [Sgourou2013] experiments (purple and green resp.).

These new simulations support that two different forms have been stabilized in different experiments. Namely, the *B form* by Lavrov *et al.* [Lavrov1999] and the *C form* by Sgourou *et al.* [Sgourou2013]. The latter is found to be the ground state in DFT-based calculations by many

different groups [Liu2002, Zirkelbach2011, Sgourou2013b, Wang2014], and the fact that it dissolves at room temperature in the experiment of Lavrov [Lavrov2018] is puzzling.

We suggest that the observation of two different complex forms can be explained by two different experimental set-ups. The first main difference is the irradiation condition (particles and temperature) which is electrons at 10K in the experiment of Lavrov *et al.* [Lavrov1999] and neutrons at 350K in the one of Sgourou *et al.* [Sgourou2013]. The oxygen concentration is the second important difference, coming from the grade of silicon being Float-Zone and Czochralski respectively. As a consequence of the high oxygen concentration in the latter experiment, most of the produced vacancies have been quickly inactivated by the formation of VO complexes. On the opposite, a higher concentration of free vacancies after irradiation in the former experiment is a possible source of dissolution of the C_iC_s .

To summarize, in this Reply, we reaffirm that the form identified as the G center by Lavrov *et al.* [Lavrov1999] is the *B form* given the new provided range of frequencies together with our KMAL simulations of the dissociation of the G center. We also confirm that the *C form* is the ground state for C_iC_s and is formed during both irradiation conditions. However, it can be partly or completely annihilated during and after irradiation by the fast diffusing vacancies created during the same irradiation. Finally, we propose a simple way to distinguish the two forms based on their dissociation temperatures that differ of more than 100°C.

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