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Electron paramagnetic resonance of molecular hydrogen in silicon

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Stallinga, Gregorkiewicz, and Ammerlaan Reply:

From our paper [1] we quote: “*The particular issue of a possible Si-NL52 \leftrightarrow P_b relation clearly requires further insight and is currently under investigation.*” Such further studies have indeed been carried out [2]. On the basis of spectroscopic research by magnetic resonance, strong similarities between the NL52 and P_b centers are found. Here, in addition to the same symmetry type and nearly identical g values and the hyperfine structure constants, we have found yet one more important clue; namely also the superhyperfine interaction with silicon neighbors was found to be identical for both centers [2]. On the other hand, significant differences between the two spectra cannot be overlooked. The most obvious difference is the presence of a small hyperfine interaction related to hydrogen for NL52, but absent in case of P_b . A nonspectroscopic major difference is found in the production conditions: the P_b center requires oxygen for its formation [Si/SiO₂ interface (SIMOX)], whereas the NL52 center is generated by hydrogen implantation in the bulk of oxygen-lean material. In order to account for all observations some complex defect modeling will certainly be required.

A Reply more specifically to the issues raised in the Comment [3] might include the following facts and opinions.

The general classification of paramagnetic centers according to their spin-Hamiltonian parameters, e.g., as proposed by Lee and Corbett [4], is of empirical indicative character. A similar estimation can be applied to theoretical indications which cannot reject an experimental model. Calculations by Chang and Chadi and others [5] predict a $\langle 111 \rangle$ -oriented interstitial H₂ molecule as the lowest-energy configuration. Theoretical evaluation of the influence of the distorted environment has not yet been performed.

The proposed identification of the Si-NL52 center as the (decorated) hydrogen molecule is, for the greater part, based on the varying intensity ratio of the dominant hyperfine structure of the spectrum; to our knowledge, this is a unique feature never before encountered for a defect center in silicon. The investigations show that this ratio changes for experimental conditions even below saturation. For conditions approaching saturation, the intensities of the NL52 spectral components tend to exhibit a 1:2:1 ratio (Ref. [2], Fig. 2). Such a value should indeed be expected if the ortho-para conversion took place as the hydrogen nuclear spins become decoupled by the strong microwave field. On the other hand, for a ²⁹Si hyperfine interaction [6], this would represent a discrepancy by a factor of ≈ 20 . In the situation when the final, ENDOR-based, identification of the nucleus responsible for the dominant hyperfine interaction as either ¹H or ²⁹Si is missing for *both* the NL52 and P_b spectra, the recent work has concentrated on this unique phenomenon. Other

arguments, among them also those linking the observed electron paramagnetic resonance spectra with particular deep-level transient spectroscopy measurements, must be considered as circumstantial only.

Finally, we would like to reiterate that the P_b center has been observed until now exclusively for environments with an extremely high concentration of oxygen, sufficient to form SiO₂. Such conditions are definitely not available in the bulk of samples where the NL52 spectrum has been generated. Further, the hydrogen decoration, a very plausible interpretation suggested in the Comment, has never been reported in the numerous experiments on the hydrogenation of the P_b centers; in all of these studies passivation with loss of P_b signal, and not decoration with conversion of P_b to NL52 signal, has been reported. In the most recent contribution of the subject [7] the authors argue that the P_b center can be passivated and again activated by atomic hydrogen. Following the proposed reinterpretation of our data one would have to assume that the same center can be generated, passivated, and decorated by atomic hydrogen. It is difficult to see how all the three processes could be (alternatively) possible. The correct model should offer an explanation for these findings.

While clearly more studies are necessary to propose a unified P_b -NL52 model, a possible explanation could involve a mechanism in which the roles of oxygen and hydrogen would be interchanged, with two hydrogen atoms substituting for one oxygen. Although plausible, such a mechanism is at the moment highly speculative and remains to be corroborated.

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