

Comment on "Electron Paramagnetic Resonance of Molecular Hydrogen in Silicon"

Stallinga, Gregorkiewicz, Ammerlaan, and Gorelinskii report the discovery of a new paramagnetic defect (NL52) in hydrogen-implanted and annealed silicon which they identify as a negatively charged $\langle 111 \rangle$ molecular hydrogen interstitial in silicon [1]. We discuss first the inconsistencies in this identification and then propose an alternative model.

The measured magnitudes and anisotropies of the Zeeman and dominant hyperfine tensors associated with the NL52 center are characteristic of a Si dangling-bond type of defect. These characteristics have been established previously [2,3]. It is not apparent how Stallinga *et al.* have considered this information in arriving at their model for the NL52 center. Stallinga *et al.* have not corroborated their claim by showing the *dominant* hyperfine spectrum that would arise from the D_2^- center, a distinctly different spectrum characterized by five hyperfine lines. Stallinga *et al.* base their model for the NL52 center on the anomaly in the measured intensity of the dominant hyperfine lines (Ref. [1], Fig. 1); such anomalies should be confirmed by measurements in slow passage without saturation.

There are also strong indications that the H_2 molecule in the silicon lattice does *not* give rise to a paramagnetic state. This has been found from both first-principles pseudopotential-density-functional calculations [4] and *ab initio* molecular orbital calculations [5]. The H_2 molecule is located at the tetrahedral interstitial site, oriented in the $\langle 100 \rangle$ direction (although other orientations are very close in energy), with a bond length of 0.82 Å. There is no evidence for any level in the band gap; that is, the neutral state is the only stable charge state of the molecule. An examination of the band structure and the wave functions show that the H_2 -induced levels are so far removed from the band edges as to make capture of a carrier impossible. In the negative charge state the extra electron does not occupy the H_2 antibonding orbital. Rather, it resides in the lowest silicon antibonding (conduction-band-like) state. Perturbations in this basic defect structure due to the proximity of other atoms are unlikely to change the diamagnetic nature of the center.

As Stallinga *et al.* point out, the NL52 Zeeman and the dominant hyperfine interactions in terms of spectral line positions are very nearly identical to those of the P_b center associated with the (111) Si-SiO₂ interface [1], whose identity as a $\langle 111 \rangle$ dangling bond localized on a surface silicon atom is based on extensive experimental and theoretical work [6,7]. Because of the essentially identical nature of these two spectra, we propose that the NL52 center is a hydrogen decorated P_b -like center. It might be associated with bubbles resulting from the hydrogen implantation. In this model the dominant hyperfine splitting would arise from the defect Si atom on which the dangling

bond is mostly localized, and the H superhyperfine splittings observed by Stallinga *et al.* (Ref. [1], Fig. 3) would be due to neighboring hydrogen atoms.

Conversely, assigning the P_b center to H_2^- centers, as might be inferred from the work of Stallinga *et al.*, is inconsistent with other experimental results. For example, the P_b center exhibits two levels in the silicon band gap: the positive/neutral and the neutral/negative charge state transitions; its neutral charge state, which is slightly below the middle of the band gap, is paramagnetic. Consequently, in the model of Stallinga *et al.* the upper diamagnetic state of the P_b center would then be H_2^{2-} , a charge state even less likely than H_2^- . Furthermore, extensive microscopic studies concerning the hydrogen passivation and dissociation of the P_b center, which are highly consistent with the Si dangling bond model, are virtually impossible to explain with an H_2 model for the P_b center [6,8].

K. L. Brower and S. M. Myers

Sandia National Laboratories
Albuquerque, New Mexico 87185-0974

A. H. Edwards

Department of Electrical Engineering
University of North Carolina
Charlotte, North Carolina 28223

N. M. Johnson and Chris G. Van de Walle

Xerox Corporation
Xerox Palo Alto Research Center
Palo Alto, California 94304

E. H. Poindexter

U. S. Army Research Laboratory
Electronics and Power Sources Directorate
Fort Monmouth, New Jersey 07703-5601

Received 7 February 1994

PACS numbers: 76.30.-v, 33.35.Ex

- [1] P. Stallinga, T. Gregorkiewicz, C. A. J. Ammerlaan, and Y. V. Gorelinskii, Phys. Rev. Letters **71**, 117 (1993).
- [2] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).
- [3] Y.-H. Lee and J. W. Corbett, Phys. Rev. B **8**, 2810 (1973).
- [4] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10791 (1989); C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).
- [5] A. H. Edwards (to be published).
- [6] See review articles in Semiconductor Science and Technology (1989).
- [7] M. Cook and C. T. White, Phys. Rev. Lett. **59**, 1741 (1987); Phys. Rev. B **38**, 9674 (1988).
- [8] K. L. Brower and S. M. Myers, Appl. Phys. Lett. **57**, 162 (1990); K. L. Brower, Phys. Rev. B **42**, 3444 (1990); **38**, 9657 (1988).

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.

P. Stallinga, T. Gregorkiewicz, and C. A. J. Ammerlaan
van der Waals-Zeeman Laboratorium
University of Amsterdam
The Netherlands

Received 22 March 1994

PACS numbers: 76.30.-v, 33.35.Ex

- [1] P. Stallinga, T. Gregorkiewicz, C. A. J. Ammerlaan, and Yu. V. Gorelinskii, Phys. Rev. Lett. **71**, 117 (1993).
- [2] P. Stallinga, T. Gregorkiewicz, and C. A. J. Ammerlaan (to be published).
- [3] K. L. Brower *et al.*, preceding Comment, Phys. Rev. Lett. **73**, 1456 (1994).
- [4] Y. H. Lee and J. W. Corbett, Phys. Rev. B **8**, 2810 (1973).
- [5] K. J. Chang and D. J. Chadi, Phys. Rev. B **40**, 11 644 (1989); J. W. Corbett, S. N. Sahu, T. S. Shi, and L. C. Snyder, Phys. Lett. **93A**, 303 (1983).
- [6] K. L. Brower, Appl. Phys. Lett. **43**, 1111 (1983).
- [7] J. H. Stathis and E. Cartier, Phys. Rev. Lett. **72**, 2745 (1994).