

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

Stallinga, Gregorkiewicz, Ammerlaan, and Gorelkinskii 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].

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