Comment on "Inverted Order of Acceptor and Donor Levels of Monatomic Hydrogen in Silicon"

In a recent Letter [1], Johnson, Herring, and Van de Walle (JHV) have concluded that interstitial H in Si has two energy levels in the gap, the acceptor level being *lower* than the donor level, implying that H is a negative-U impurity. The $(0/+)$ level—associated with H at the bond-centered (BC) site (H_{BC}^{0} and H_{BC}^{+})—is placed near $E_c - 0.2$ eV by deep-level transient spectroscopy (DLTS) [2] measurements, a value close to that recently obtained from RF-μSR experiments [3] and has now been established.

The $(-/0)$ energy level of H—associated with H_T^- and H_{BC}^0 according to JHV—has been deduced to be exactly midgap on the basis of the measurement of capacitance transients which JHV observe after shining light on hydrogenated, phosphorous-doped samples. The following is assumed. (a) Under illumination, at room temperature, in a depleted region, the neutral {P,H} pair captures two holes, forming H^+ and P^+. (b) After flooding the depleted region with electrons, H^+ captures two electrons and forms H^-. (c) A spontaneous conversion of H^- to H^+ then occurs by emission of two electrons. To be more specific, it is assumed that "if the system makes a transition from H^- to H^0, it will coast downhill to the global minimum at BC." (d) The position of the acceptor level is obtained via JHV's Eq. (4) from measurements of the electron capture time τ_c from capacitance transients.

We would like to point to the following inconsistencies. (1) Despite repeated attempts by two of us (C. H. S. and R. A. A.), the capacitance transients reported by JHV have not been seen. These transients are the key to their claim that H^+ is mobile and swept out of the depletion region after illumination, and that H^- is produced by electron capture after debonding. Our experiments [4] included measurements on P- and As-doped Si, with Pd and Pt Schottky metallizations. (2) The assumption that under illumination all or most {P,H} pairs break up into a mobile H^- (and a P^+) is not supported by experiment. As has been reported in an earlier study [5], the donor reactivation reaction is 30–80% *reversible.* This reversibility has also been observed for all the samples tested when trying to reproduce the reported transients. We previously suggested [6,7] that {P,H} pairs may convert to a charged $\{\mathrm{P,H}\}^+$ defect or that H debonds from P and is trapped at a nearby (unidentified) site that becomes positively charged. Thus, the electron emission and capture processes reported by JHV do not necessarily involve monatomic interstitial hydrogen. (3) The assumption that only three states of H are present, H^- (at the T site), H^0 (at the BC site), and H^+ (at the BC site), is incorrect. With the exception of one study [8], there is agreement among theorists [9] that H^0 is metastable in Si. μSR experiments show that two paramagnetic centers coexist. One corresponds to a neutral muonium atom on the average at the T site (Mu_T^0). The other is stable, has trigonal symmetry, and is at the BC site ($\mathrm{Mu}_{\mathrm{BC}}^0$). Both centers survive in doped samples, and recent experiments [3] show that in n-type Si the Mu_T^0 species plays a role in the diffusion of muonium above 400 K. The activation energy for the $\mathrm{Mu}_T^0 \rightarrow \mathrm{Mu}_{\mathrm{BC}}^0$ transition is estimated [3] to be 0.4 eV. Since the zero-point energy of a proton is smaller than that of a muon, the activation energy for the $\mathrm{H}_T^0 \rightarrow \mathrm{H}_{\mathrm{BC}}^0$ transition is certainly larger than 0.4 eV. Thus, the result of the reaction $\mathrm{H}_T^- \rightarrow \mathrm{H}^0 + e^-$ is first the metastable H_T^0 state. A (possibly large) fraction of H_T^0's will convert to $\mathrm{H}_{\mathrm{BC}}^0$, then ionize to become $\mathrm{H}_{\mathrm{BC}}^+$. The charge state conversions are therefore more complicated than assumed by JHV, casting doubt on the validity of the assumptions (a) and (b) in the manuscript.

We emphasize that this Comment does not address the negative-U issue itself. RF-μSR experiments [3] tentatively place the acceptor level associated with $\mathrm{Mu}_T^{(-/0)}$ near $E_c - 0.4$ eV, which is below the donor level.

C. H. Seager and R. A. Anderson
Division 1111, Sandia National Laboratories
Albuquerque, New Mexico 87185

S. K. Estreicher
Physics Department, Texas Tech University
Lubbock, Texas 79409-1051

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