

Energy Level of the 0 to + Charge Transition of Substitutional Manganese in Silicon

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An energy level of $E_v + 0.38$ eV related to the 0 to + charge transition of substitutional manganese in silicon has been determined with a combination of deep-level-transient spectroscopy and ESR measurements. There is no evidence for ordinary amphoteric or negative- U behavior in the lower half of the band gap. This is the first identified energy level of a 3d substitutional impurity in silicon.

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There is a long tradition of exploring the properties of 3d (iron group) transition-metal point defects in silicon (see, for example, Weber¹ and references therein). Earlier calculations of the charge-transition levels including spin polarization and electronic relaxation were applied only to interstitial 3d elements.² Recently, advanced self-consistent calculations using a spin-unrestricted linear-muffin-tin Green's function method were carried out and expanded to substitutional 3d elements.^{3,4} Dependable data concerning the energy levels of the interstitial site could be determined by use of deep-level transient spectroscopy (DLTS) in combination with Hall and ESR measurements.⁵⁻⁸ Regarding the substitutional 3d elements, however, no well-identified data were available so far. Thus the value of the 0 to + charge-transition level of substitutional manganese presented in this paper can serve as a first check of the validity of existing theories when applied to substitutional 3d transition metals, and might give valuable hints for further investigations.

To form substitutional manganese, samples were made from 1.7- Ω cm p -type silicon by application of a copper-manganese codiffusion technique as reported by Ludwig and Woodbury.⁹ Successfully prepared samples show the typical ESR fingerprint [manganese nuclear spin (MNS)] of single positively charged substitutional manganese.⁹ The X-band spin-resonance first-derivative absorption signal shown in Fig. 1 exhibits full cubic symmetry. The twofold spin degeneracy ($S=1$) is lifted by interaction with the manganese-nuclear-spin system ($I=\frac{5}{2}$), leading to a 2×6 line splitting. The Hamilton parameters ($g=2.0259$, $A=-63.09 \times 10^{-4}$ cm⁻¹) are different from those of a signal, possessing the same manifold and symmetry, which is attributed to negatively charged interstitial manganese.⁹

All samples containing substitutional manganese produce both the MNS signal and a DLTS¹⁰ peak exhibiting an energy level of 0.38 ± 0.01 eV as derived

from the Arrhenius plot of the DLTS spectra measured at different lock-in frequencies. Reference samples prepared with copper diffusion but without manganese codiffusion show no detectable 0.38-eV peak. On the other hand, samples could be produced that show the MNS signal and contain only the 0.38-eV transient with no other visible residual peaks. A correlation plot (Fig. 2) shows the unambiguous proportionality between the ESR signal intensity, obtained by double integration of the MNS signal, and the corresponding calibrated DLTS peak height. Each point is gained from an individual sample with a different concentration of substitutional manganese, prepared by variation of the diffusion and quenching conditions. Isochronal-annealing experiments observing both the ESR signal and the DLTS peak height after each 30-min annealing step show a marked decrease in the intensities at about 450 °C. The comparatively high annealing temperature deviates significantly from the

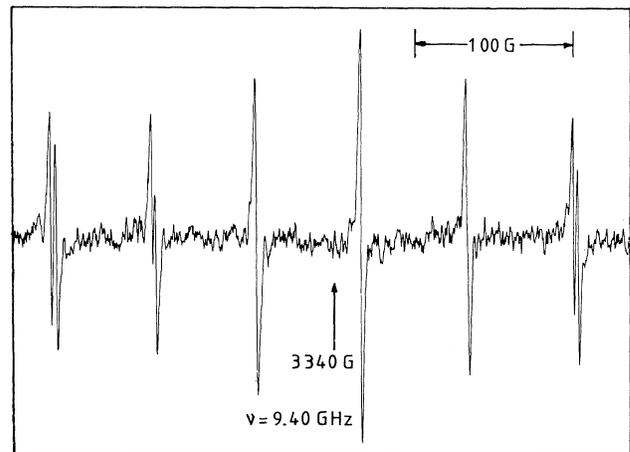


FIG. 1. ESR first-derivative absorption signal of single positive substitutional manganese in arbitrary orientation.

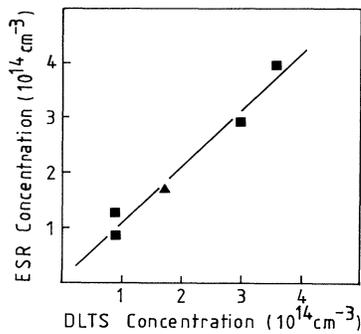


FIG. 2. Correlation plot of the 0.38-eV DLTS peak intensity and the integrated ESR intensity of the MNS signal. The triangle corresponds to the phosphorus calibration sample.

normal annealing properties of interstitial $3d$ impurities. Preliminary measurements of the defect migration energy yield an approximate value of greater than 2 eV, supporting the assumption of the substitutional site.

Since the MNS signal is even visible in p -type samples with high background doping concentration, causing the Fermi level to pin to the shallow doping level at sufficiently low temperature, we conclude that there is no $+$ to $++$ transition level above the background doping level. Furthermore, if a $-$ to 0 transition level would exist between the middle of the band gap and the 0 to $+$ transition level, a second transient of equal intensity but remarkably different time constant should appear in the DLTS spectra of our samples. There is no evidence for it, and so we argue that the 0 to $+$ transition level is the only one in the lower half of the band gap. However, the possibility of a negative- U situation with the $-$ to 0 transition level situated between the 0 to $+$ level and the shallow doping level has to be considered. If so, the transition from the metastable neutral to the single negative state is masked by the slower $+$ to 0 transient in the DLTS signal and we should have observed one individual transient with twice the amplitude compared to a normal $+$ to 0 transition. To check this case a careful calibration of both the spin density and the DLTS defect concentration of a single sample was performed by use of a phosphorus spin standard. The spin concentration was $1.7 \times 10^{14} \text{ cm}^{-3}$, from which value the DLTS calibration differed only by 5%. Therefore we conclude that there is no negative- U situation in the lower half of the band gap. Thus, we attribute the 0.38-eV DLTS level to the 0 to $+$ charge transition of substitutional manganese.

Finally, we would like to discuss these results in the light of the existing theory. Figure 3 shows the one-electron-level scheme of neutral substitutional manganese and the derived many-electron charge-

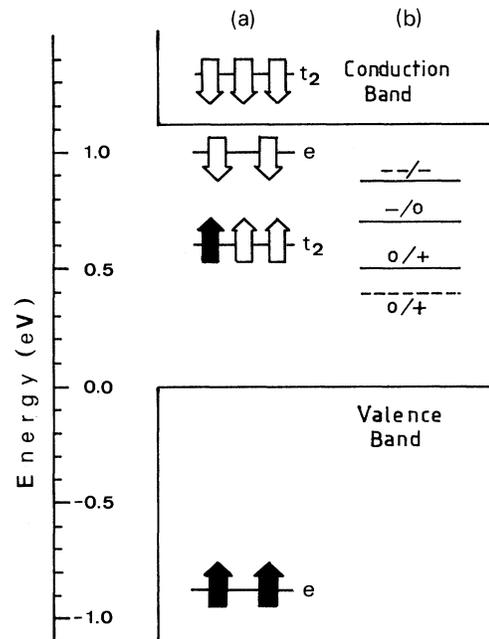


FIG. 3. (a) One-electron-level energies of neutral substitutional manganese (the occupied states are visualized by full arrows) and (b) charge-transition levels. The solid lines are calculated by Beeler, Andersen, and Scheffler, and the dashed line represents our experimental value.

transition levels reported in the up-to-now most advanced paper of Beeler, Andersen, and Scheffler.⁴ With the exception of chromium, manganese is the only substitutional impurity with a high spin state predicted by this theory and in accord with the Ludwig-Woodbury scheme.⁹ The singly positive state used in our ESR correlation can be derived from the neutral one-electron configuration by removal of the t_2 electron. This leads to a $S=1$ singlet spin state due to the doubly occupied e level deep in the valence band. Considering the low concentration of substitutional manganese obtainable by diffusion techniques (see above), the high spin-lattice relaxation of the neutral and single negative triplet states explains the negative history in finding the corresponding ESR spectra. Since there is agreement between experiment and theory concerning the 0 to $+$ donor level (0.38 and above 0.50 eV above the valence band, respectively), we can expect a similar agreement for the single and double acceptor levels predicted to be located about 0.40 and 0.20 eV below the conduction band, respectively. From the corresponding states, the double negatively charged singlet state has already been observed by Ludwig and Woodbury.⁹

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