

Comment on "Neutralization of Shallow Acceptor Levels in Silicon by Atomic Hydrogen"

An interesting phenomenon has recently been reported by Pankove *et al.*,¹ namely the neutralization by reaction with atomic hydrogen of electrically active shallow levels due to boron in silicon. The object of this Comment is to point out that the evidence in that report was not conclusive as presented, and requires clarification in a number of areas.

Firstly, the observed increase in resistivity is seen for plasma exposure temperatures up to 300°C.¹ The proposed B⁻H⁺ pairs of Sah, Sun, and Tzau² cited as a precedent are fully dissociated at 185°C. Similarly, the resistivity of the samples in Ref. 1 is only returned to its original value by vacuum annealing at 500°C—these cannot be the same centers.

Secondly, the spreading resistance profiles in Ref. 1 do not follow any expected hydrogen distribution for simple, one-species diffusion into silicon. In the case of hydrogen being trapped at defect sites to which it can bond, the hydrogen concentration at X would follow

$$H(X) = H_0 \exp\left[\frac{-x}{D^{1/2}/[d]k}\right],$$

where H_0 is the surface hydrogen concentration, D is the diffusivity of atomic hydrogen, $[d]$ is the density of trapping sites, and k is a reaction constant. The reported hydrogen permeation depth at 122°C would lead to a diffusion coefficient of atomic hydrogen of $\sim (2-7) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, based on a simple $(Dt)^{1/2}$ calculation. This is an order of magnitude higher than previously measured H-bulk diffusivities measured at the same temperature in material of the same doping density.³ Some mention should be made of the depth dependence with time of the resultant neutralization effect.

Thirdly, the characteristics of the silicon exposed to the hydrogen plasma were not given, a potentially serious omission. For example, crucible-grown silicon contains swirl defects which may act as gettering sites for metallic and other impurities. Hydrogenation of these,⁴ rather than the bulk boron, would lead to an increase in resistivity of the sample. The role of other species in the plasma was not clarified—other experiments indicate that both hydrogen and oxygen are involved in the B deactivation mechanism, i.e., B⁻OH⁺ centers are

formed.⁵ Electrolytic doping with H alone and H plasma exposures (both with samples in or out of the discharge) have been unsuccessful in producing an effect. Because of the interference effect from the high ¹H and ¹⁶O backgrounds in secondary ion mass spectrometry apparatus (and the high O concentration in Czochralski-grown Si), unambiguous detection of the incorporation of these species requires their labeling by the use of ²H and ¹⁸O plasmas. To achieve adequate sensitivity using ¹H, the B level in the samples would need to be extremely high—under these conditions the hydrogen diffusivity would be very small indeed and the experiment would be most uncertain.

Fourthly, one cannot use deep-level hydrogenation experiments as precedents for shallow-level hydrogenation. The perturbations introduced in the host lattice are totally different, and while deep levels might be expected to bind hydrogen quite tightly, there is no reason to suggest boron would do the same.

Fifthly, the small doping efficiency of boron in hydrogenated amorphous silicon can be explained by boron-defect complex formation, as found in high-dose boron-implanted single-crystal silicon⁶—one does not need a B-H interaction.

In summary, the reported observation of hydrogen passivation of boron levels in silicon cannot be regarded as conclusive without further, more specific, evidence.

S. J. Pearton
AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received 20 April 1984
PACS numbers: 71.55.Fr, 72.80.Cw

¹J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, *Phys. Rev. Lett.* **51**, 2224 (1983).

²C. T. Sah, J. Y. C. Sun, and J. J. Tzau, *Appl. Phys. Lett.* **43**, 204 (1983).

³J. M. Kahn, S. J. Pearton, and E. E. Haller, *Bull. Am. Phys. Soc.* **29**, 208 (1984).

⁴S. J. Pearton and A. J. Tavendale, *Phys. Rev. B* **26**, 7105 (1982).

⁵W. L. Hansen, S. J. Pearton, and E. E. Haller, *Appl. Phys. Lett.* **44**, 606 (1984).

⁶D. Fink, J. P. Biersack, H. D. Carstanjen, F. Jahnel, K. Muller, H. Ryssel, and A. Osei, *Radiat. Eff.* **77**, 11 (1983).