

(1957).

⁵A. Honig, Quantum Electronics-Resonance Phenomena Conference, September, 1959 (Columbia University Press, New York, 1959), p. 450.

⁶For a purer sample (about 10^{14} P/cm³), larger photocurrent enhancements were obtained upon filling the P⁺ traps with electrons. The question arises as to

whether a superior photodetector can be made with the double-illumination technique. For background-limited photodetectors, an improvement in the signal-to-noise ratio is possible when the background and signal are in different spectral regions. We would like to thank Dr. Henry Levinstein for discussion of this point.

VACANCY INTERACTIONS IN SILICON

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The production and properties of vacancies in silicon are subjects upon which much empirical work has been done. For the most part the interpretation of the data in terms of detailed models has been inconclusive. Recently the interaction of radiation-induced defects (suggested to be vacancies) with chemical impurities has been demonstrated.¹ In this Letter, experiments of a new type are described which demonstrate that vacancies do indeed interact with certain chemical impurities. These experiments involve the trapping and annihilation of vacancies by interstitial impurities which thereby become substitutional. The effect has been detected by spin resonance techniques for the impurities manganese and chromium; vacancies were introduced into silicon by the precipitation of copper or silver, or by electron irradiation. The experiments involving Cu and Mn will be described first, followed by a brief description of those involving Cu and Cr, and of the irradiation experiments.

Manganese has been previously detected in Si in the forms Mn⁻ and Mn⁺⁺. Samples have now been prepared in a manner similar to that previously described² except that Cu as well as Mn is alloyed and diffused into the samples. When such samples are cooled relatively slowly, two new spectra are seen due to isolated Mn, one in *n*-type and the other in *p*-type material. It is proposed that if only Mn is introduced and if the sample is quenched sufficiently rapidly, the Mn is in interstitial sites. On the other hand, in samples which also contain copper, vacancies are created during the quenching. These vacancies are annihilated by the interstitial Mn with most of the Mn becoming substitutional. In *n*-type silicon containing an excess of phosphorus, the substitutional Mn is in the form Mn⁻. In *p*-

type silicon containing an excess of boron, the substitutional Mn is in the form Mn⁺.³ A summary of the spin resonance results for the four isolated forms of Mn is given in Table I.

The resonance measurements indicate that the Mn in each of these cases is in a tetrahedral crystalline environment as an isolated impurity. The two negatively charged species of Mn are both seen in the presence of uncompensated phosphorus, indicating that they are not different charge states of one impurity site, but represent different sites. There are only two different sites which show the tetrahedral symmetry of the host lattice, the substitutional site and the interstitial site. Thus one species must be substitutional and the other interstitial. Similar arguments apply to the two positively charged species, since each is seen in silicon containing an excess of boron.

A dramatic difference between Cu-doped and Cu-free samples is the stability of the resonance center. For example, the Mn⁺⁺ spectrum dis-

Table I. Electron spin resonance parameters for four isolated species of Mn in Si. *S* is the electron spin, *a*, the cubic field interaction parameter, and *A*, the (isotropic) hyperfine interaction parameter of the Mn nucleus. Both *a* and *A* are expressed in units of 10^{-4} cm⁻¹.

Ion	Interstitial		Substitutional	
	Mn ⁺	Mn ⁻	Mn ⁺	Mn ⁻
<i>S</i>	5/2	1	1	5/2
<i>g</i>	2.0066	2.0104	2.0259	2.0058
<i>a</i>	+19.88	+26.1
<i>A</i>	-53.47	-71.28	-63.09	-40.5

appears in a few days if samples are left at room temperature. Even when samples are stored at dry ice temperature, a decline in intensity is observed. In contrast, the Mn^+ spectrum has been observed with little decrease in intensity in a sample left at room temperature for 18 months. The greater stability of the Mn^+ site is strong evidence that it is the substitutional site while the Mn^{++} site is the interstitial. Consistent with this the Mn^- site is more stable than the Mn^- site. Further evidence that the Mn in the Cu-free sample is interstitial is its ability to diffuse at room temperature to form clusters of four Mn atoms and to form pairs with acceptor atoms.² Only interstitial ions would be expected to exhibit such room temperature mobility since vacancies are normally not present. Finally, a consistent picture⁴ of the d -shell configurations and electron spin values can be made on the basis of the substitutional-interstitial assignments proposed here.⁵

Although the mechanism by which the Cu creates vacancies is not certain, several interesting possibilities exist. The solubility of copper at the diffusion temperature is about $10^{18}/cm^3$, while only $5 \times 10^{14}/cm^3$ has been detected electrically.⁶ Presumably the rest of the copper precipitates when the sample is cooled. If a sufficient number of Cu atoms are substitutional at the diffusion temperature, vacancies may be formed by a (substitutional) \rightarrow (vacancy + interstitial) \rightarrow (vacancy + precipitate) mechanism as the sample is cooled. Another possibility, proposed to us by Dash, is that Cu precipitates strain the crystal, causing the formation of dislocation loops as found by Parasnis and Mitchell in $AgCl$.⁷ The motion of these loops through the crystal then produces the needed vacancies. It is noted that silver will also convert Mn in silicon to substitutional sites. Other impurities may act similarly.

Similar experiments have been performed on Cr-doped silicon. Chromium has been previously detected² as an interstitial in the form Cr^+ . If both Cr and Cu are introduced into material that initially has high resistivity, a new spectrum is seen, which is attributed to substitutional Cr^0 . The observed spin is 1.

When silicon containing interstitial Cr is irradiated with 1.5-Mev electrons (total flux of approximately $6 \times 10^{16}/cm^3$), the same center is created that is observed in silicon doped with both Cr and Cu. The samples were kept below $175^\circ K$ during the irradiation and were warmed to room temperature for a short period following the irradiation (less than 30 minutes for one sample). Thus vacancies are produced by the irradiation which can be trapped by interstitial Cr. The experiments to date indicate that vacancies are mobile at room temperature and probably lower.⁸ This is consistent with the results of Watkins *et al.*¹

The authors thank W. C. Dash for helpful discussions and J. W. Corbett for irradiating samples. C. R. Trzaskos assisted in the experimental work.

¹G. D. Watkins, J. W. Corbett, and R. M. Walker, *J. Appl. Phys.* **30**, 1198 (1959); G. Bemski, *J. Appl. Phys.* **30**, 1195 (1959).

²H. H. Woodbury and G. W. Ludwig, *Phys. Rev.* **117**, 102 (1960).

³The assignment of the charge state for these ions follows from the observation that neither resonant form is observed in material which had high resistivity before diffusion. This means that the difference in charge state of the Mn ion in phosphorus-doped material and boron-doped material must be at least two. However, the difference is odd since the observed spin is even for one ion and odd for the other. Thus, the charge states must differ by at least three electrons. The assigned charge states are the lowest consistent with these requirements.

⁴G. W. Ludwig and H. H. Woodbury, following Letter [*Phys. Rev. Letters* **5**, 98 (1960)].

⁵The new observations presented in this Letter on Mn plus the fact that many of the arguments as to its interstitial vs substitutional character also apply to the impurities studied in reference 2, lead us to propose that all of the impurities discussed in reference 2 are interstitial.

⁶C. B. Collins and R. O. Carlson, *Phys. Rev.* **108**, 1409 (1957).

⁷A. S. Parasnis and J. W. Mitchell, *Phil. Mag.* **4**, 171 (1959).

⁸These experiments do not preclude the possibility that vacancies diffuse as di-vacancies or as some other complex.