PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PHYSICS OF SEMICONDUCTORS, KYOTO, 1966
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 21, SUPPLEMENT, 1966

XIII-9. Effect of Doping on the Electron Spin Resonance in Phosphorus Doped Silicon

H. KODERA

Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo, Japan

Effect of doping on the electron spin resonance in phosphorus doped silicon was investigated. At liquid helium temperature, a resonance line was observed at the center of the hyperfine structure in samples of fairly high phosphorus concentration and only the central line remained at higher donor concentration and temperatures. The *g*-value and the line width were functions of the phosphorus concentration. The central line was identified with fairly free electrons, including conduction electrons. The line width was considered to be determined by the impurity scattering and a spatial extent covered by the movement of electrons.

§ 1. Introduction

Most of the electron spin resonance studies in silicon have been concerned with electrons or holes localized on various lattice defects.[1] A few experimental works have been reported on conduction electrons.[2]

In the present work, electron spin resonance experiments were carried out at room, liquid nitrogen and liquid helium temperatures on *n*-type silicon doped with various amounts of phosphorus. At liquid helium temperature, a resonance line was observed at the center of the hyperfine structure in samples of fairly high phosphorus concentration and only the central line remained at higher donor concentration and temperatures. The *g*-value and the line width were measured as a function of phosphorus concentration. Some part of the experimental results at room and liquid nitrogen temperatures have been already reported, showing that the observed electron spin resonance is related with the electrical conduction.[3,4] The present study, as a whole, has confirmed the relation between the electron spin resonance and the electrical conduction. The following model is proposed for the absorption line at room and liquid nitrogen temperatures and the central line at liquid helium temperature: (1) the resonance is due to fairly free electrons, especially at higher donor concentration and/or temperatures, they are conduction electrons; (2) the line width is determined by the impurity scattering and a "mean free path" corresponding to the spatial extent covered by the movement of electrons.

§ 2. Experimental

Experiments were carried out at room, liquid nitrogen and liquid helium temperatures, using an *X*-band ESR spectrometer. The samples were powdered silicon doped with phosphorus, whose concentration was determined from the room temperature resistivity measurement and ranged from 7×10^{16} to $5\times10^{19}\,\mathrm{cm}^{-3}$. The surface resonance was eliminated by etching the pulverized samples in the mixture of hydrofluoric and nitric acids.

At liquid helium temperature, a resonance line appears at the center of the hyperfine structure in samples of fairly high phosphorus concentration and only the central line remains for the phosphorus concentration higher than $10^{18}\,\mathrm{cm}^{-3}$. At room and liquid nitrogen temperatures, only a single line is observed corresponding to the central line at liquid helium temperature. The line shape of the central line was found to be Lorentzian independent of temperature and phosphorus concentration, while that of the hyperfine lines Gaussian.

The *g*-value and the line width of the central line were measured as a function of phosphorus concentration as shown in Figs. 1 and 2. The *g*-value at room temperature decreases monotonically with increasing donor concentration, while at liquid nitrogen temperature, it is approximately constant up to a certain donor concentration. At liquid helium temperature, the concentration range, where the *g*-value is constant, becomes wider than that at liquid nitrogen temperature. The line width at room temperature increases monotonically with the donor con-

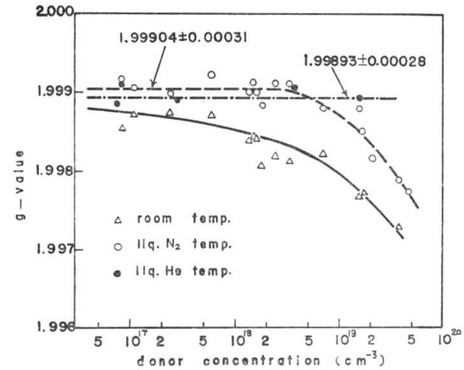

Fig. 1. Dependence of *g*-value on the donor concentration in phosphorus doped silicon.

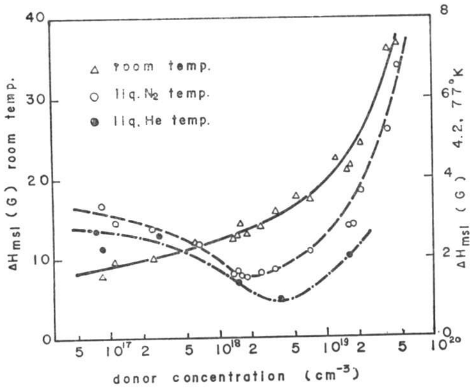

Fig. 2. Dependence of line width on the donor concentration in phosphorus doped silicon.

centration, while at liquid nitrogen and liquid helium temperatures, it shows a minimum.

The absorption intensity of the central line was measured at room and liquid nitrogen temperatures by comparing with the absorption signal from the known amount of DPPH. In order to estimate the number of spin in a silicon sample, it is desirable that the rf magnetic field acting on the sample is the same as that acting on the reference. The reference sample DPPH was deposited on the inner wall of a quartz tube which was used to hold the powdered silicon sample. The effective spin density, N^*, is defined as the number of DPPH molecules which yield the absorption of the same intensity. Assuming that the absorption intensity is proportional to the paramagnetic susceptibility, the effective spin density is related with the density of conduction electrons, n, as

$$N^* = n\frac{F'_{1/2}(\eta)}{F_{1/2}(\eta)}\,. \tag{1}$$

In the above equation, $F_{1/2}$ the Fermi integral,

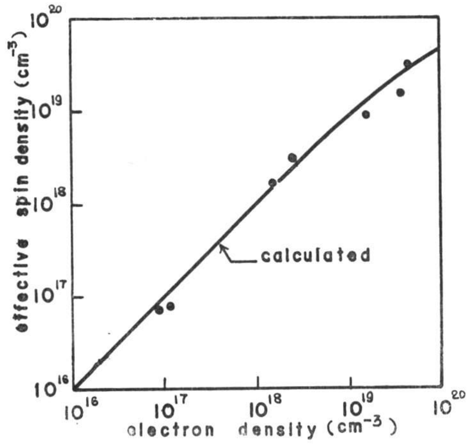

Fig. 3. Effective spin density at room temperature plotted against the electron density.

$F'_{1/2}$ its first derivative and η the reduced Fermi energy. One-to-one correspondence between the number of spin and conduction electron was confirmed at room temperature, as shown in Fig. 3. At liquid nitrogen temperature, the qualitative agreement was found only at higher donor concentration.

Resonance behaviors of the hyperfine structure and the central line were compared at liquid helium temperature in the same sample where both were observed. They were found to be different in the following respects.

(1) The *g*-value of the central line is larger by an amount

$$0.00019 \pm 0.00012.$$

(2) The line width of the central line changes with the donor concentration, while that of the hyperfine lines is constant.

(3) The line shape of the central line is Lorentzian in contrast to the Gaussian hyperfine structure.

(4) The hyperfine lines easily saturates as compared to the central line.

§ 3. Discussions

At room temperature, phosphorus atoms are completely ionized, leaving no unpaired electrons on impurity centers. Most of the electrons are excited into the conduction band at liquid nitrogen temperature, if the donor concentration exceeds $10^{18}\,\mathrm{cm}^{-3}$. Combined with the calculation of the degeneracy temperature, the electron spin resonance at room and liquid nitrogen temperatures are considered to be due to the non-degenerate and degenerate conduction electrons respectively. According to the theory of the electron spin resonance of conduction electrons,[5,6] the ratio of the line width to the square of the g-shift is a linear function of the reciprocal of the impurity scattering mobility μ_I.

$$\frac{\varDelta H_{msl}}{(\varDelta g)^2}=A\left(\frac{1}{\mu_I}+\frac{f}{\mu_L}\right) \tag{2}$$

$$\frac{\varDelta H_{msl}}{(\varDelta g)^2}=A^*\left(\frac{c^{2/3}}{\mu_I}+\frac{f^*}{\mu_L}\right) \tag{3}$$

Equation (2) holds for the nondegenerate conduction electrons and eq. (3) for the degenerate ones.[4] In the above equations, μ_L stands for the lattice scattering mobility, c the impurity concentration and coefficients A, f, A^* and f^* are constant at a fixed temperature. As is seen in Fig. 4, qualitative agreement was found between the theory and experiment, showing that the increase of the line width is attributable to the ionized impurity scattering.

Electrical conductivity measurements at liquid helium temperature[7,8] have shown that, if the phosphorus concentration exceeds $4\times10^{18}\,\mathrm{cm^{-3}}$, the electrical conductivity is fairly high on account of the formation of impurity band. The central line at liquid helium temperature will be identified with conduction electrons, if the donor concentration is higher than that of the minimum line width. The increase of the line width may be attributed to the impurity scattering. On the other hand, the electrical conductivity is quite low in samples of such lower donor concentration that both hyperfine structure and the central line are observed. Although the low electrical conductivity and the presence of the hyperfine structure suggest that most of the electrons are localized on impurity centers, the central line

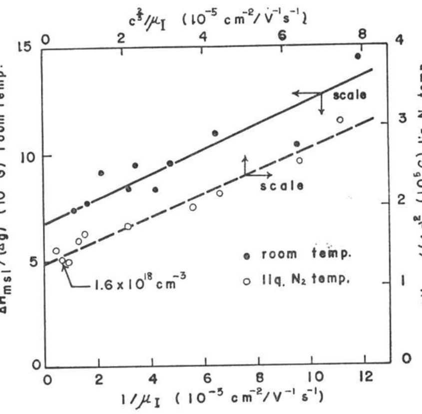

Fig. 4. Comparison with the theory of the electron spin resonance of conduction electrons.

may not be considered to be due to localized electrons because of the difference in the resonance behaviors. The g-value of the central line is constant from the lower concentration where the hyperfine structure is observed to the higher concentration where electrons are considered to move freely through the impurity or conduction band. Then the central line, for such lower donor concentration, should be identified with fairly free electrons. The electrons, however, cannot move so freely as they are in the conduction or impurity band. They are trapped in the neighborhood of several phosphorus atoms and moving from one phosphorus atom to another one. The line width will be determined by a "mean free path" which corresponds to a spatial extent covered by the movement of electrons, resulting in the decreasing line width with the increasing donor concentration. This will be the case also with the experiment at liquid nitrogen temperature.

Any model has never been proposed for the concentration dependence of g-values. The effect of temperature on the concentration dependence suggests that the spread of the electron energy due to thermal motion would be one of the possible causes.

§ 4. Conclusions

A single absorption line was observed at room and liquid nitrogen temperatures and a line at the center of the hyperfine structure at liquid helium temperature. They are identified with fairly free electrons. At room temperature, the line width increases with the donor concentration and the resonance absorption is ascribed to conduction electrons. At liquid nitrogen and liquid helium temperatures, the line width shows a minimum at a certain donor concentration. The resonance absorption is attributable to electrons in the conduction or impurity band for the donor concentration higher than that of the minimum line width. The increase of the line width is explained by the impurity scattering. At lower concentration and temperatures, electrons are able to move only in a limited spatial extent and the line width will be determined by a "mean free path" corresponding to the limits of movement.

The author wishes to express his sincere thanks to Profs. Y. Uemura and H. Hasegawa for their valuable discussions. He is greatly indebted to Dr. K. Narita for his suggestion of the method of analysis and Dr. H. Kusumoto for his hearty guidance and discussions in the experimental work. His thanks are due to Dr. S. Maeda and Mr. T. Hirai for their grateful encouragement throughout the work.

References

1) G. W. Ludwig and H. H. Woodbury: *Solid State Physics* ed. F. Seitz and D. Turnbull (Academic Press, 1962) Vol. 13, p. 223.
2) A. M. Portis, A. F. Kip, C. Kittel and W. H. Brattain: Phys. Rev. **90** (1953) 988; G. Feher: Phys. Rev. **114** (1959) 1219; G. Lancaster, J. A. van Wyk and E. E. Schneider: Proc. Phys. Soc. (London) **84** (1964) 19.
3) H. Kodera: J. Phys. Soc. Japan **19** (1964) 915.
4) H. Kodera: J. Phys. Soc. Japan **21** (1966) 1040.
5) Y. Yafet: *Solid State Physics* ed. F. Seitz and D. Turnbull (Academic Press, 1963) Vol. 14, p. 1.
6) R. J. Elliott: Phys. Rev. **96** (1954) 266.
7) G. A. Swartz: J. Phys. Chem. Solids **12** (1960) 245.
8) C. Yamanouchi: Meeting at the Institute for Solid State Physics of Tokyo University, June, 1965.

DISCUSSION

Geist, D.: The resonance of holes in B shows a similar benaviour: A decrease in line width from 800 down to 77°K. But an increase to yet lower temperatures (1.5°K). Further, there is a dependence of line width on the doping element, C, Si or Be. This shows that the holes cannot be considered to be free in the usual sense. Therefore, I should ask whether anything is known about the influence of the doping element on the line width in doped Si.

Kodera, H.: My work has been done especially on the P doped Si. However in the preliminary experiment it was found that the width became quite large in As or Sb doped Si, enough to make it very difficult to observe the resonance signal at room temperature. Dr. Schneider has reported that the line width of the As doped Si is large at liquid nitrogen temperature as compared with the P doped Si.

Maekawa, S.: We observed the susceptibility by ESR technique in P doped Si. In the non-metallic sample, at 77°K, the observed value is much larger than the estimated value for conduction electrons. This suggests that the resonance absorption is due also to localized electrons in hopping motion as well as the conduction electrons. In the metallic sample, the observed value is also larger than that estimated for conduction electrons. So it seems to us localized electrons will contribute to resonance absorption in any case.

Kodera, H.: I have discussed only the qualitative nature of the resonance behavior showing that the central line is ascribed to free electrons. Although most of the present experiments are explained by the free electron model, quantitative disagreement with the theory was encountered in many cases, and also some of the experimental results, such as the concentration dependence of the g-value, have not been explained. The presence of the localized spin might be one of the possible causes for the facts which cannot be explained by the free electron model.