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Detection of Phosphorus in Epitaxial Silicon by EPR

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Electron Devices Division
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Prepared for
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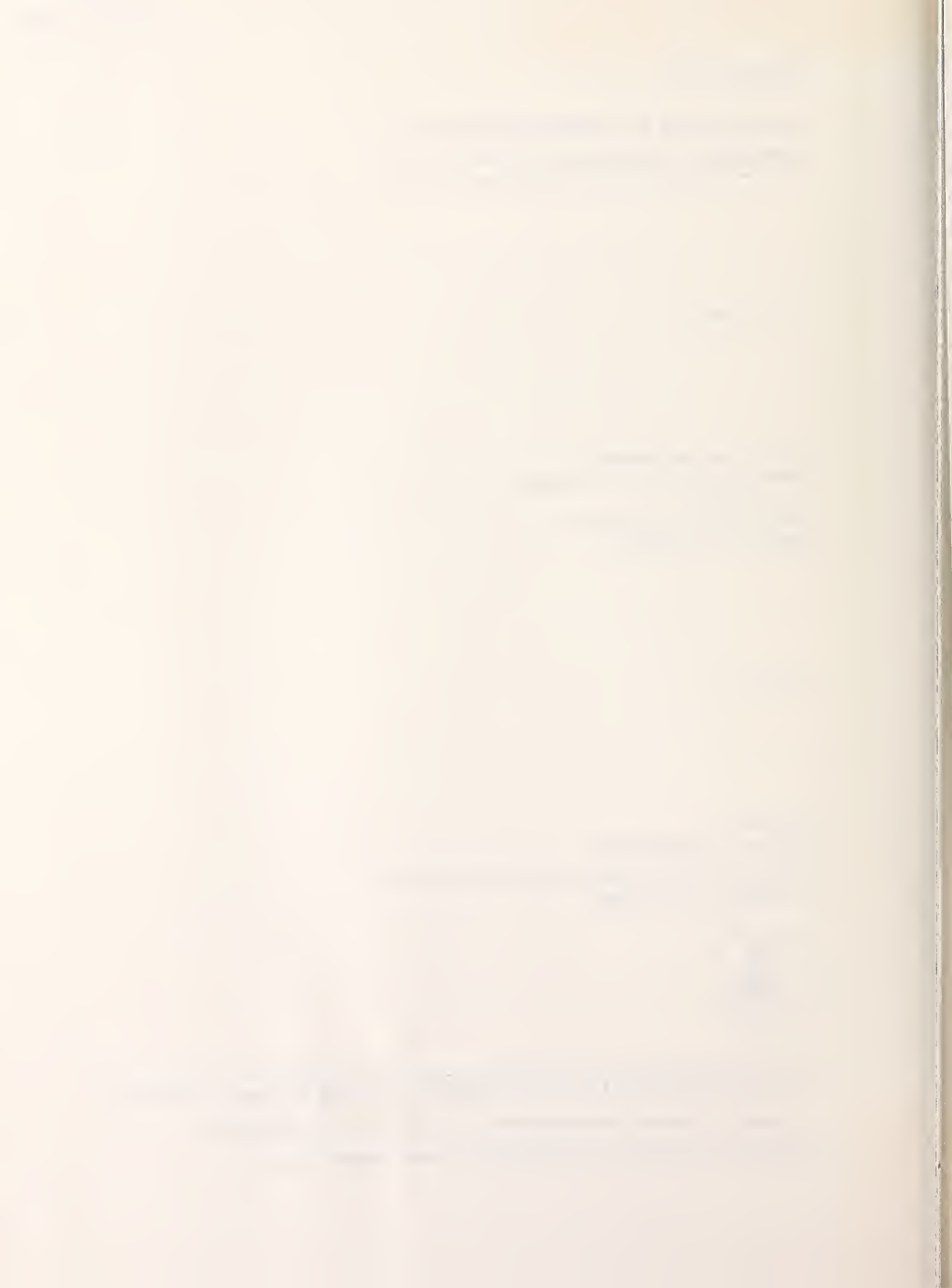


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ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy has been used to identify phosphorus in an epitaxial layer of silicon. The concentration of phosphorus atoms was estimated using a ruby standard sample (NBS SRM 2601) to establish a calibration for the spectrometer. The concentration obtained with EPR is in satisfactory agreement with the concentration obtained from Hall-effect data on the same specimen.

Key Words: Electron paramagnetic resonance; epitaxial silicon; Hall-effect measurements; phosphorus in silicon.

1. INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy has been demonstrated to be a useful tool for identifying impurities in semiconductors and for estimating their approximate concentration [1]. This report describes an application of EPR to the identification of an unintentional impurity in an epitaxial layer of silicon. A 1-mil (0.025-mm) thick epitaxial layer grown by liquid phase epitaxy on a 14-mil (0.36-mm) thick substrate of high resistivity p -type silicon was examined. The layer was grown from indium solution, but otherwise not intentionally doped. The conductivity of this epitaxial layer was determined to be n -type. Since the growth conditions would be expected to yield an epitaxial layer saturated with indium and thus have p -type conductivity, an analysis of the material was required to determine the source of the observed n -type conductivity. The two-layer Hall technique developed by Larrabee and Thurber [2] applied to this material strongly suggested that phosphorus was responsible for the n -type conductivity. Data presented in this report represent a search for the EPR signature of phosphorus from this epitaxial layer. The spectroscopic EPR results confirm that

the impurity giving rise to the n -type conductivity is indeed phosphorus as inferred from the Hall data.

11. BACKGROUND

A few aspects of EPR spectroscopy that are essential for the identification of phosphorus ions in silicon will be described briefly in "liberal terms". For a rigorous and complete treatment of the subject, there are excellent treatises available [3].

a. Unpaired Electrons in Magnetic Field.

When an unpaired electron is placed in a magnetic field, the magnetic dipole moment of the electron will align itself either parallel or anti-parallel to the magnetic field. Hence, there are two energy states (see figure 1). The spacing between the two states is given by

$$h\nu = g\beta H \quad (1)$$

where h is Planck's constant, ν is the transition frequency, g is the Landé spectroscopic splitting factor, β is the Bohr magneton, and H is the external magnetic field. In a transition between the two states electromagnetic energy of frequency ν will be absorbed or emitted. Since the frequency and the external magnetic field can be measured, and since h and β are universal constants, the value of g can be determined experimentally. For free electrons, $g = 2.0023$, which corresponds to a transition of $\nu = 9.5$ GHz at a magnetic field of about 3420 gauss.* Conduction electrons in silicon are subject to the crystalline field and therefore behave according to the band structure of the crystal. They are not free, and the g -factor is different from that of the free electrons. The best measured value [4] is

$$g_{CE} = 1.99875 \pm 0.00010. \quad (2)$$

This difference in g -value will shift the resonance magnetic field about 8 gauss at a resonance frequency of 9.5 GHz.

*"Gauss" is a customary unit to measure magnetic field in EPR spectroscopy. "Gauss" has the same magnitude as "Oersted" in vacuum, which is equivalent to 10^{-4} Tesla.

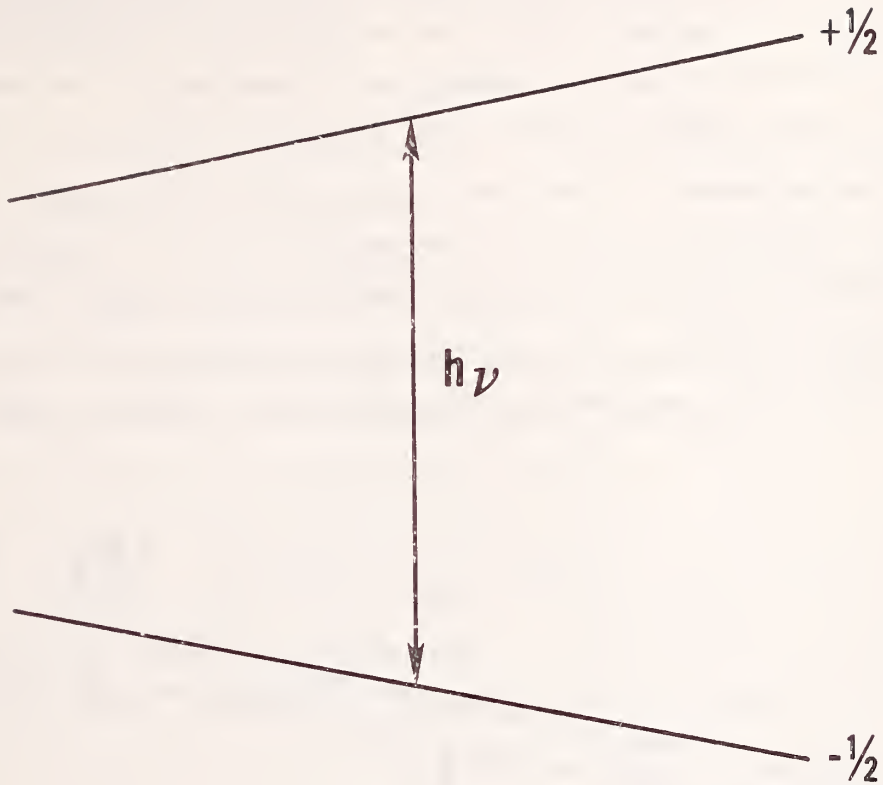


Figure 1. The Zeeman energy level diagram of an unpaired electron. The horizontal axis is the magnetic field, the vertical axis is the energy, both in arbitrary units.

b. Localized Conduction Electrons in *n*-type Si.

At low temperatures (4.2 K or below), the conduction electrons in silicon are bound in large orbits around the positive charged donor ions, in a fashion analogous to hydrogen atoms. The *g*-factor is not the same as that of the non-localized conduction electrons, and there is also a slight difference among the cases when the donors are phosphorus, arsenic, or antimony. However, these differences are small and the shift in magnetic field is only a fraction of a gauss.

Through the Fermi contact potential [5], the localized conduction electrons will interact with the donor nuclei. The electronic energy levels will be further split. In the case of phosphorus, because the nuclear spin is 1/2, each energy level will be split into two as shown in

figure 2. During an electronic transition, the nuclear states usually do not change. Thus two transitions are possible as indicated in figure 2, and the selection rules $\Delta M_S = \pm 1$, and $\Delta M_I = 0$ are obeyed. The EPR spectrum should appear as two absorption lines.

In the case of arsenic, since the nuclear spin is $3/2$, each of the electronic levels will be split into four ($2I + 1 = 4$). The spectrum should appear as four lines of equal separation and equal intensity.

For antimony, the isotopic distribution is 57.25% spin $5/2$, and 42.75% spin $7/2$ [6]. The spectrum should appear as six lines and eight

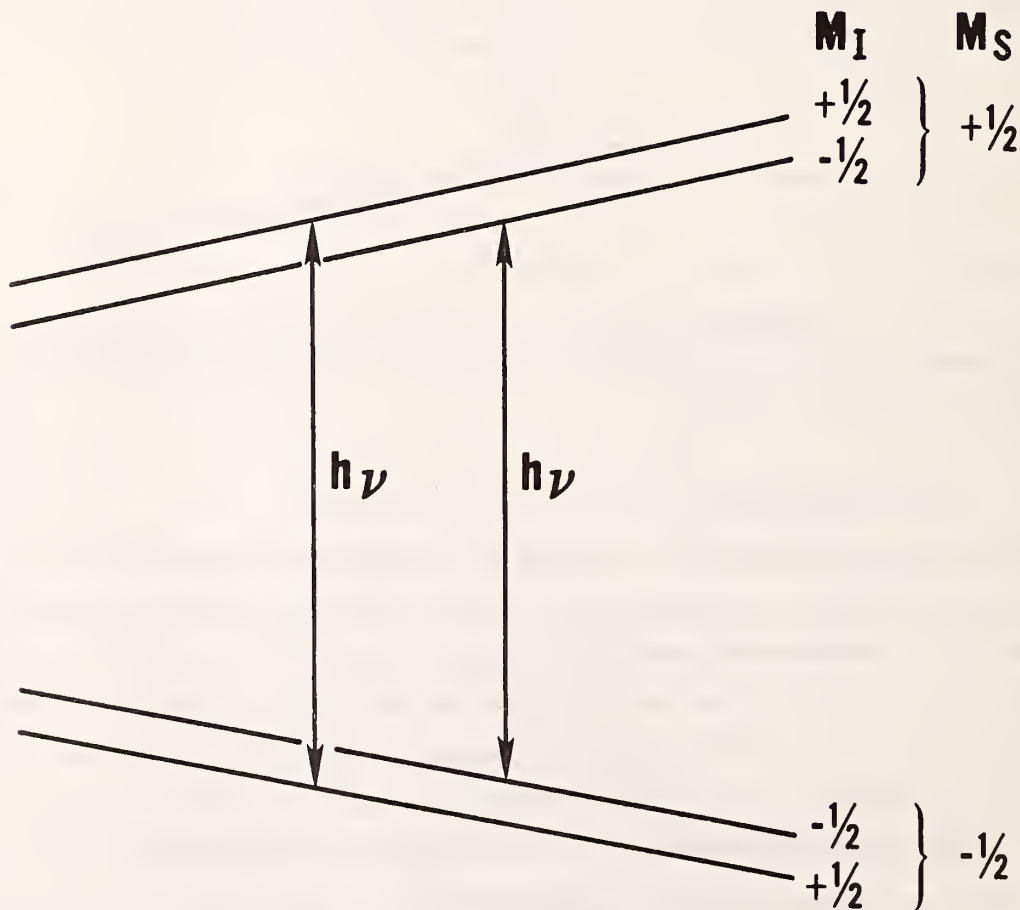


Figure 2. The Zeeman energy level diagram of an electron associated with a nucleus of spin $1/2$. M_S is the magnetic quantum number of the electronic spin, M_I is the magnetic quantum number of the nuclear spin.

lines superimposed. The members of the six line group should be about twice as intense as the members of the eight lines.

III. EXPERIMENTAL RESULTS

The EPR spectrometer is of conventional homodyne design, operated at 9.5 GHz. All the experiments were performed at a temperature of 4.2 K. The spectrometer is able to detect the EPR absorption from a sample of 10^{11} active spins provided the corresponding EPR absorption line is one gauss wide. From Hall measurements, the concentration of phosphorus ions in the epitaxial layer was estimated to be about 10^{17} cm^{-3} . The specimen available for EPR experiments was about 0.25 cm^2 in area, and the epitaxial layer was about $2.5 \times 10^{-3} \text{ cm}$ thick. The total number of spins available to be detected in the specimen was thus estimated to be about 6×10^{13} . However, since there are two phosphorus lines, and each is about three to four gauss wide, it was necessary to operate the spectrometer near the limit of its sensitivity and some experimental precautions were required.

First, the spectrometer was operated using a specimen of phosphorus-doped silicon in which the total number of phosphorus ions was known to be about 10^{15} . The characteristic spectrum of electrons bound to phosphorus ions was observed as shown in figure 3. The two hyperfine lines as discussed above are resolved; the spacing about 40 gauss. The weak absorptions between the two lines are due to the clustering of phosphorus ions, that enables the orbit of the electron to enclose two or more phosphorus ions. From these observations, the range of the resonance magnetic field and the expected pattern of the absorption lines was known.

The specimen of the silicon epitaxial layer was then placed in the sample cavity of the spectrometer along with a ruby standard sample [7]. The ruby SRM has a total of $1 \times 10^{16} \text{ Cr}^{3+}$ ions with spin 3/2. A weak transition of Cr^{3+} (the active specie of the ruby SRM) was selected, the intensity of which is about 0.003 of the major ($1/2, -1/2$) transition. This spectral line of the SRM is equivalent in strength to 3×10^{13} spins. The spectrometer could register this transition as

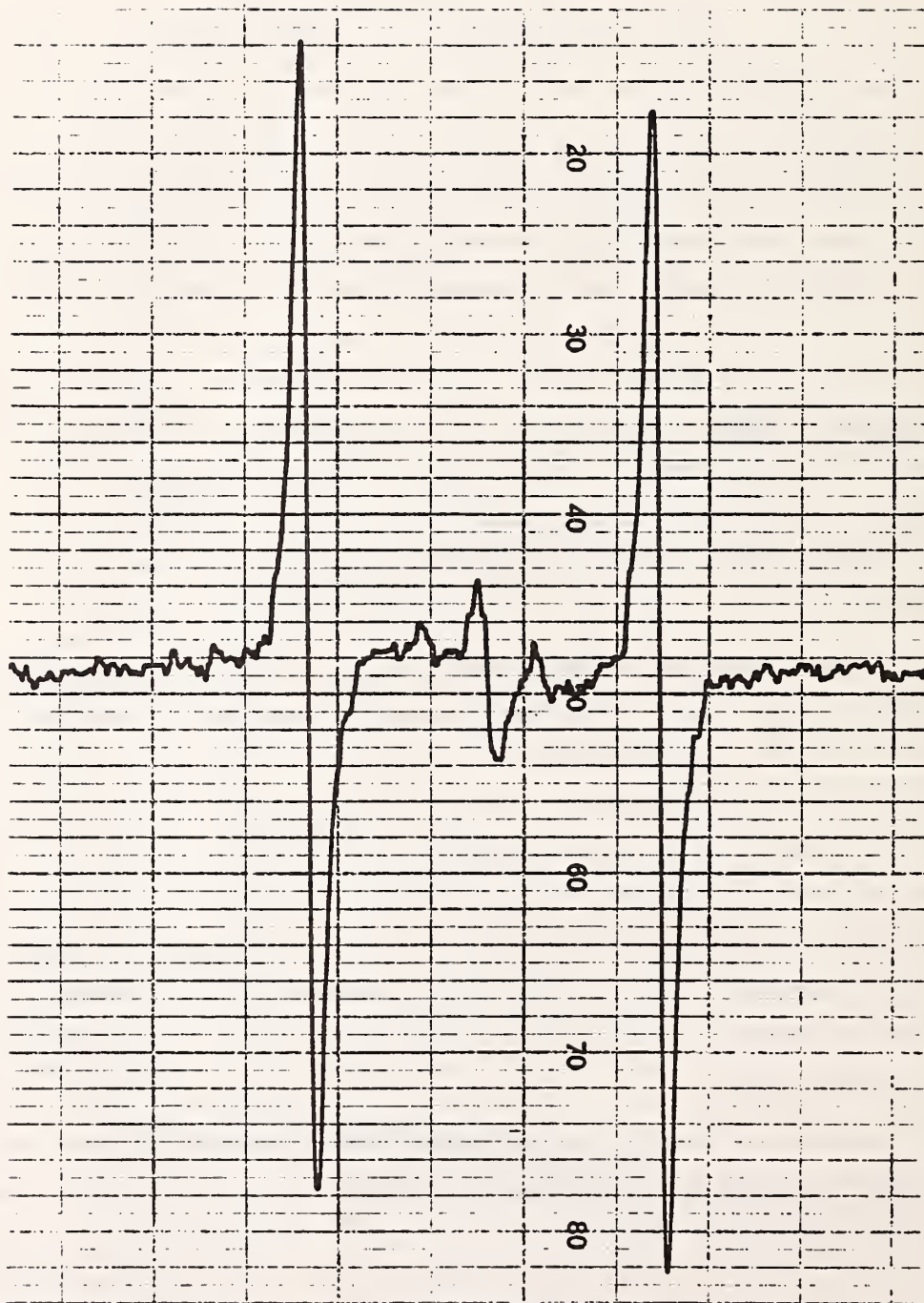


Figure 3. The EPR spectrum from phosphorus doped silicon. The temperature is 4.2 K.

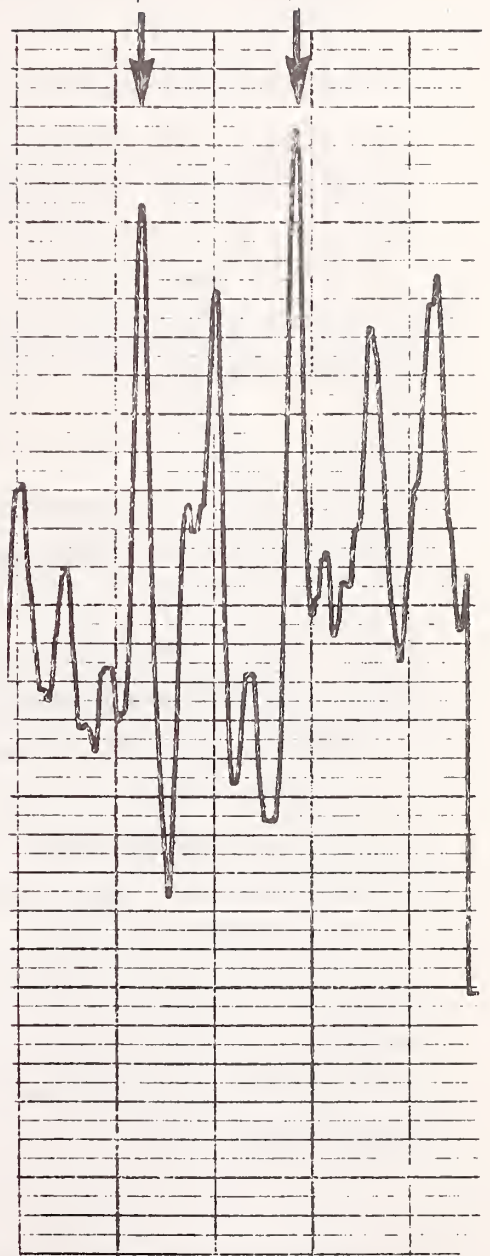
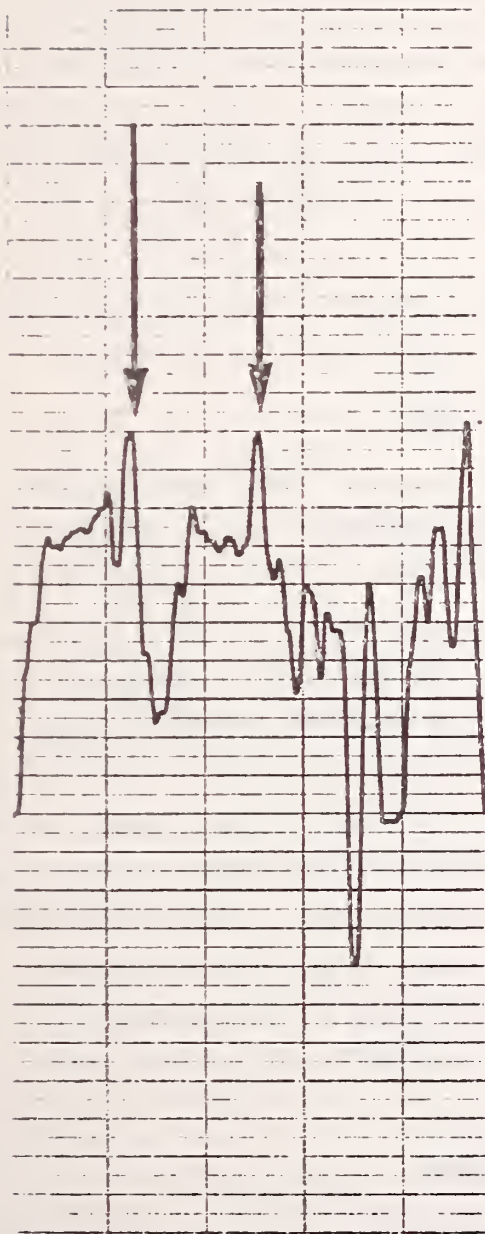


Figure 4. The EPR spectrum from the epitaxial layer of indium doped silicon. The arrows point to the peaks identified as the contribution from phosphorus ions.

a full scale signal. Then the desired range of the magnetic field for the phosphorus resonance was searched with a slow sweeping rate (~ 1 G/min), and a long lock-in amplifier integration time (10 s).

The signal from the epitaxial layer was observed under the above conditions. The results of the two best sweeps are shown in figure 4. The arrows point to the phosphorus signal, the intensity of which is about one tenth of that of the selected transition of the ruby SRM. The backgrounds are not random. They may be the contribution from clustered phosphorus ions, non-localized conduction electrons, or other donors in the layer.

IV. CONCLUSION

The presence of phosphorus ions in the epitaxial layer was confirmed from the result of this experiment. The concentration of phosphorus ions was estimated to be about 10^{16} cm^{-3} from the intensity of the EPR line. Since the signal was weak and the background intense, an accurate measurement of the concentration was not possible. The lines were about ten gauss wide, which is broader than that from the reference sample. This may be due to the fact that the spins are residing in a thin layer, or some unknown mechanism may broaden the EPR absorption lines. It may be possible that the contributions from some of the spins are too broad to be observable. Because of these considerations, it is conceivable that the estimate of the concentration could be off by an order of magnitude, and hence the 10^{16} cm^{-3} value should be considered as a lower bound, in satisfactory agreement with 10^{17} cm^{-3} from the Hall measurements [2].

V. ACKNOWLEDGEMENT

Dr. Barbara E. Sumner of the Night Vision and Electro-optics Laboratory, Ft. Belvoir, VA provided the specimen studied in this report and useful technical discussions. Technical discussions with R. D. Larrabee and W. R. Thurber are also gratefully acknowledged.

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