Phosphorus-doped Silicon

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March 18, 1997

Abstract

Elemental crystalline silicon, with its small intrinsic carrier concentration of 1.5 x 10^{10} cm^{-3} at 300K, is not capable of achieving current densities that would make it desirable as a material out of which to construct a semiconductor device. The doping of silicon with small amounts of electrically active, valence-five phosphorus donor atoms turns silicon into an n-type semiconductor with an electrical conductivity many orders of magnitude higher than its undoped value. The doping of silicon, with phosphorus in particular, is of interest to applied physicists because phosphorus, when in silicon, acts as a "getter" of various contaminants, especially mobile alkali ions, which if unchecked can destabilize the long-term performance of semiconductor devices. Phosphorus-doped silicon is also of interest to condensed matter theorists because of its curious behavior at the metal-insulator transition. The study of its behavior has inspired and continues to inspire even to this day refinements of and corrections to Fermi liquid theory.

1 Crystal and Electronic Structure

The two most common non-elemental semiconductor types are the "III-V" and the "I-VI" semiconductors, that is, those that combine elements from the third and fifth groups of the periodic table, such as InSb and GaAs, and those that combine the second and sixth groups, such as ZnO and CdS. Phosphorus-doped silicon is in neither of these large groups. It is a combination of a group IV-a (silicon) with a V-a (phosphorus) element. Germanium, like silicon, is also in group IV-a, and like silicon, it also has a valence of four and is frequently doped with phosphorus.

Two of the many ways to dope a host lattice with phosphorus are by implantation and diffusion. In implantation, phosphorus is sent at high kinetic energy into the lattice, using an intense electric field, which sometimes generates structural defects in the process. A gentler way is by simply diffusing phosphorus into silicon, a process which can also introduce defects.

Once inside, phosphorus loses (donates) its most weakly bound electron to the conduction band of silicon, becoming a positively charged phosphorus ion "core". It entirely replaces a silicon atom at a former silicon atom site, forming one of the most popular types of covalent bonds, the tetrahedral bond (popular because of its sp^3 hybrid orbitals), with four silicon atom neighbors, as shown in Figures 1 and 2.

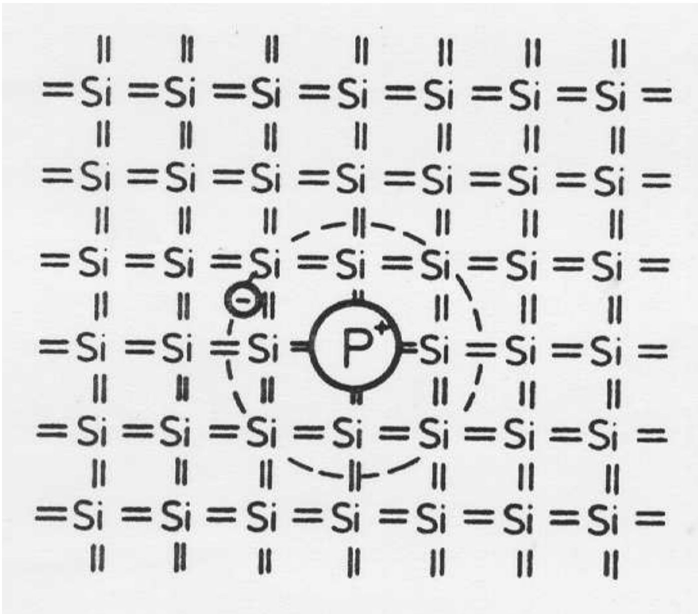

Figure 1. The positively-charged phosphorus ion entirely replaces a silicon atom and donates its free electron to the conduction band.

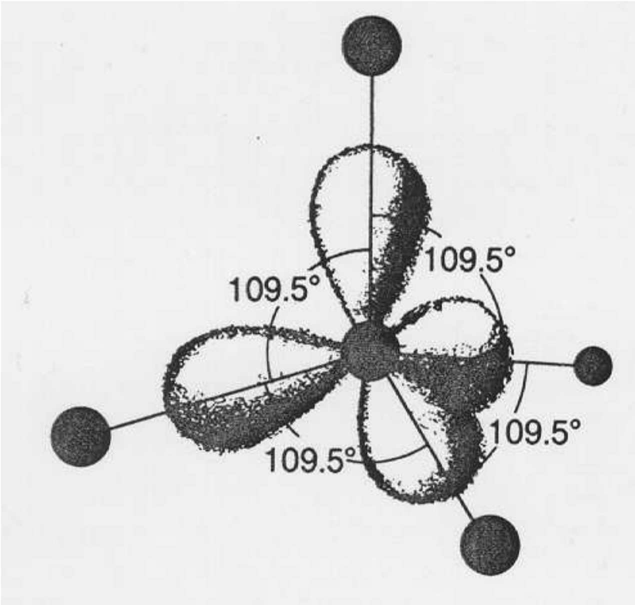

Figure 2. One of the most popular types of covalent bonds is the tetrahedral, popular because of its sp^3 hybrid orbitals.

The sp^3 hybrid orbitals are popular because of their high packing density and net gain in energy despite the energy used to perform the promotion required by this type of bond of one 2s electron into a higher 2p orbital. Many substances besides phosphorus-doped silicon which also contain sp^3 hybrid orbitals also show semiconductor activity.

2 Phosphorus as a Getter in Silicon

Alkali ions and other contaminants can be present in newly-manufactured semiconductor devices without causing problems initially. They are introduced by the manufacturing process itself, even if the doped silicon used in their production was initially free of them. Over time, these mobile ions migrate slowly due to forces exerted on them by electric fields produced by applied voltages experienced during the device's operation, especially if these applied voltages are large or if the device has also been exposed to high temperatures. After several years, these semiconductor devices, especially those incorporating MOSFETs, develop a drift in their offset or threshold voltage of up to several volts, dubbed by Horowitz and Hill "sodium-ion disease".[2] This disease can be cured by depositing phosphorus locally into susceptible regions of the device.

Alkali ions are not the only substances phosphorus incapacitates in silicon. It also renders gold and iron immobile. Phosphorus binds to gold through a typical Coulomb interaction, but how it binds to iron is not yet understood, since phosphorus and iron are both donor-type impurities and therefore are not expected to bond. However, it has been hypothesized[3] that since the covalent radius of phosphorus is approximately 3.8% smaller than the covalent radius of silicon, this small discrepancy may be enough to cause phosphorus, when in a silicon host, to form a compression or elastic strain field around itself, which helps iron bind to it.

3 Si:P as an Instigator of Revisions in Fermi Liquid Theory

The metal-insulator transition is an intensely studied second order phase transition. As the number of donors added to an insulator increase, a point is reached where enough electrons have been freed by their donor parent such that the insulator suddenly and discontinuously becomes conducting. This also occurs when acceptors are added to insulators. One example is H. Fritsche's now-famous plot[5] from 1955 of $1/T$ versus the log of resistivity for decreasing acceptor concentrations in Ge:Ga, reproduced in Figure 3.

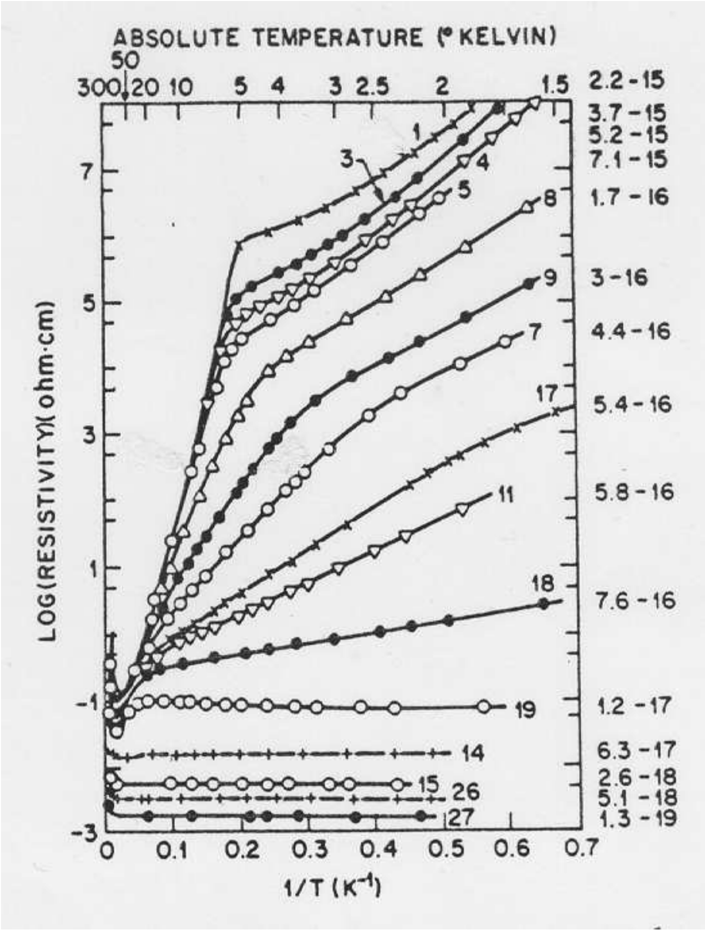

Figure 3. $1/T$ vs the log of the resistivity for decreasing acceptor concentrations in Ge:Ga.

We see in this plot that the "critical density" n_c, the density at which the phase transition occurs, for Ge:Ga is approximately 1 x 10 ^{17} cm^{-3}. Conversely, electron-electron interactions can drive a conductor into the insulating state.

The behavior of measurable quantities near either side of a phase transition is called critical behavior, and the power law relationships between these quantities are described by equations whose powers or exponents or called "critical exponents". The precise numerical values and signs of some of these exponents are a source of great controversy, and involve renormalization group equations, universality classes (quantities that share the same group of critical exponents though not their same numerical values), mean field theory, scaling theory, and a plethora of other concepts, all surrounding attempts to refine and extend Fermi liquid theory.

Why has Si:P long been central in experiments used to revise this theory? Si:P began to be studied in the early 1980's in its "dirty", eg. heavily-doped, and therefore highly disordered, form. (A high degree of disorder can be due not only to heavy doping but also to imperfections in the lattice itself.) However, it was found that it is remarkably easy to attain precise values of donor concentration in Si:P. This is important since a series of values of donor concentration is required to "sneak up on" the metal-insulator transition region. When Si:P is irradiated with neutrons, the lattice imperfections that result act as acceptors. The concentration of acceptors can then be decreased by annealing, and annealing can be done in a very precise stepwise fashion. Today, there are materials that are even easier to work with than Si:P, but since Si:P was used in so many of the preliminary experiments, it continues to be used frequently even to this day.

References

[1] Ibach, Harald and H. Luth, **Solid State Physics**, Berlin: Springer-Verlag,1995, p. 327-374

[2] Horowitz, P. and W. Hill,**The Art of Electronics**,Cambridge: Cambridge University Press, 1993, p. 400

[3] Takahashi, H. et al, "Generation and Dissociation of Complexes of Iron and Phosphorus Atoms in Silicon", J. Appl. Phys. 78 (5), 1995

[4] Schilling, F. et al, "Nuclear Magnetic Resonance Characterization of Doped SiO2 Films Used in Integrated Circuits", J. Appl. Phys. 78 (6), 1995

[5] Fritzche, H., Phys. Rev. 99, 406 (1955)

[6] Kastner, M. et al, **Disordered Semiconductors**, New York: Plenum Press, 1987, p.39

[7] Goldenfield, N., **Lectures on Phase Transitions and the Renormalization Group**, Reading: Addison-Wesley, 1992

[8] Paalanen, M. and R. N. Bhatt, "Transport and Thermodynamic Properties Across the Metal-Insulator Transition", Physica B 169 (1991) 223-230