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SULFUR IN SILICON

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1. INTRODUCTION

THE systematic study of the effects of impurities in silicon[(1)] has added greatly to our scientific and technological knowledge. Well understood is the action of the Group III elements as acceptor impurities and the Group V elements as donor impurities. As substitutional impurities in the silicon lattice, the Group VI elements are expected to be donor impurities since only four of their six outer valence electrons are needed to form tetrahedral bonds with neighboring silicon atoms. This donor action is revealed in our experiments with sulfur. Oxygen in silicon shows donor behavior,[(2)] but it appears to be active only in combination with other impurities present.[(3)] In germanium, the elements sulfur, selenium, and tellurium are donors and levels have been determined for each of them.[(4)] Donor activity has also been claimed for oxygen in germanium.[(5)]

2. PROCEDURE

The first evidence for the donor nature of sulfur in silicon was obtained by admitting some hydrogen sulphide gas into the argon protective gas during part of the growth period of a single crystal by the Czochralski technique. The crystal was grown from a *p*-type melt but it was *n*-type in the middle section in which the hydrogen sulphide gas had been present in growth. No further doping of growing crystals was attempted since diffusion proved to be a more controllable process of introducing sulfur.

In the diffusion process, less than 1 mg of 99·85 per cent pure sulfur was sealed off in an evacuated quartz tube with silicon samples of dimensions $\sim 1{\cdot}5 \times 3 \times 10$ mm^3. Times of the order of one day were sufficient to saturate these samples at high temperatures. Sulfur reacted with the silicon samples and excess sulfur in some cases caused a mass transport of the silicon and eroded the samples. There is evidence in the literature[(6)] for silicon sulfides (both SiS and SiS_2) and these probably form in an intermediate stage. Contacts to the samples were made by spring wires against gold-plated regions. The magnetic field used in the cryostat arrangement was 6000 G.

3. ELECTRICAL ACTIVITY

From measurements of resistivity and Hall coefficient over the range 80°–700°K, as shown in Fig. 1 for a typical sample, CD-490, a level of 0·18 eV from the conduction band was attributed

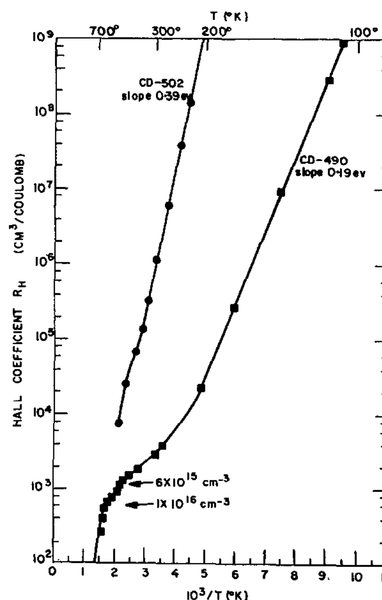

FIG. 1. Hall coefficient vs. reciprocal temperature for typical samples of sulfur-doped silicon, showing the two observed levels. Samples were *p*-type before diffusion of sulfur. The slopes of the Hall coefficient curves must be corrected for the $T^{3/2}$ dependence of the density of states near the bottom of the conduction band. This correction gives the levels as 0·18 and 0·37 eV from the conduction band edge.

to sulfur. This level was observed in samples of both floating zone and crucible grown silicon into which sulfur was diffused and also in samples cut from the one grown crystal doped with hydrogen sulfide. In addition, one *p*-type crystal was grown dominated by gallium rather than the usual acceptor, boron, and the same level was observed on diffusing in sulfur. The observed donor activity of sulfur was not dependent on the concentration or nature of the acceptor present so that an ion-pairing mechanism for the level can be ruled out.

At higher temperatures a second level is evident in CD-490 and in other samples with the 0·18 eV level, leading one to suspect that sulfur has two levels above the middle of the gap. In samples in which the 0·18 eV level is completely empty and the deeper level partially empty by compensation ($2N_S > N_A > N_S$, where N_S is the sulfur concentration and N_A the shallow acceptor concentration), then a level at 0·37 eV from the conduction band is observed, as in CD-502 of Fig. 1.

Spectroscopic analysis of the sulfur revealed that the five previously studied elements[1] which give rise to deep levels in silicon, namely iron, manganese, copper, gold, and zinc were present to less than 1 part in 10^5. Thus these elements could not be responsible for either of the levels observed. No evidence for any acceptor activity of sulfur was observed on diffusing into *n*-type samples.

4. SOLUBILITY AND DIFFUSION COEFFICIENT

Initial electrical studies at 1200°C revealed a solubility of $\sim 10^{15}$ cm^{-3} for sulfur. However, it was found that insufficient sulfur was present in these samples to saturate them, the amount of sulfur having been kept low because of its reactivity with silicon. Further samples showed that up to 3×10^{16} cm^{-3} could be introduced into silicon as plotted in Fig. 2. Retrograde solubility is evident close to the silicon melting point. Comparison of this solubility curve with HALL's curves[7] indicates that the segregation coefficient of sulfur in silicon is $\sim 10^{-5}$, of the same order of magnitude as the other deep level impurities studied. The concentration in the 0·18 eV level was approximately equal to that in the 0·37 eV level in various samples, allowing for partial compensation of the shallower level by acceptors present and for the fact that the 0·37 eV level is not completely emptied before intrinsic generation of carriers competes.

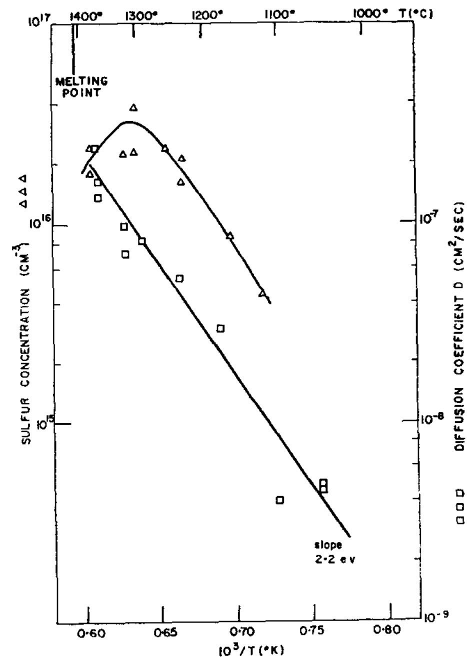

FIG. 2. Solubility and diffusion coefficient of sulfur in silicon as determined from electrical measurements.

Radiotracer studies using S^{35} did not give accurate results. The beta particles for S^{35} are so weak (0·17 MeV) that only a very thin layer of silicon is effectively counted and sample activity was close to background. The radiotracer studies do suggest, however, that the total sulfur content cannot be much more than that measured as electrically active.

The diffusion coefficient, also plotted in Fig. 2, was determined by measuring the depth of the *p-n* junction formed on diffusion of sulfur into *p*-type silicon. The surface donor concentration was determined from the solubility curve, multiplying by two to account for the two observed levels. The values of diffusion coefficient are intermediate between very fast diffusers such as copper or nickel ($D \sim 5 \times 10^{-5}$ cm^2/sec) and the Group III-V elements ($D \sim 10^{-11}$ to 10^{-13} cm^2/sec at 1200°C). The activation energy for

sulfur diffusion ($D = D_0 \exp - E/kT$) is given by the slope as 2·2 eV or 51,000 cal. This compares with $\sim$ 1 eV for iron and gold[8] and 3·5 to 4·7 eV for the III-V elements.[9] The diffusion coefficient for oxygen is $\sim 10^{-8}$ cm^2/sec at the melting point of silicon, with an activation energy of 3·5 eV.[10]

5. PHOTOCONDUCTIVITY SPECTRA

Samples in which the 0·18 eV and the 0·37 eV levels were dominant were studied using Newman's technique.[11] Results, plotted in Fig. 3,

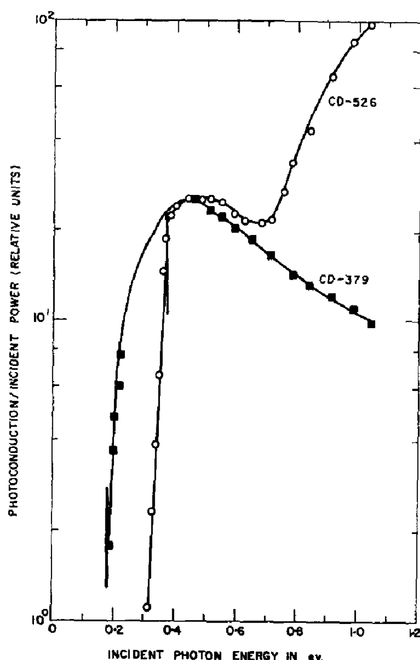

FIG. 3. Photoconductive spectra of n-type sulfur-doped silicon. Thermal ionization energies are indicated for comparison with the optical curves. The spectra were shifted vertically to coincide at 0·45 eV.

show that these spectra support the level positions determined from electrical measurements. In addition, in the sample with the 0·37 eV level, CD-526, there appears to be a very deep level, whose origin is not understood.

6. CONCLUSIONS

Sulfur introduces two donor levels into the forbidden band of silicon, at 0·18 eV and 0·37 eV from the conduction band. Its maximum solubility of 3×10^{16} cm^{-3} at 1320°C is comparable to that of iron, manganese and zinc, but diffusivity is somewhat lower. $D = 0{\cdot}92 \exp(-2{\cdot}2/kT)$, roughly $D(1300°\text{C}) = 10^{-7}$ cm^2/sec and $D(1100°\text{C}) = 10^{-8}$ cm^2/sec. The double donor activity of sulfur suggests that it is a substitutional impurity in the silicon lattice, but it presumably diffuses as an interstitial impurity. Its solubility is only $\sim$1/50 that of oxygen in silicon, but apparently oxygen is electrically active only in combination with other impurities or defects.

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