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Properties of Silicon Doped with Iron or Copper

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Iron introduces a donor level into silicon at 0.40 ev from the valence band observed both in crystals doped in the melt and in crystals into which iron was diffused at 1200°C. This level converts anomalously to a level 0.55 ev from the conduction band on standing at room temperature. The conversion is reversible in the range ~70°–200°C; above 200°C, the electrical activity of iron irreversibly disappears. No evidence for acceptor action of iron was found. The electrically active solubility of iron, 1.5×10^{16} cm^{-3} at 1200°C, is higher than the radiotracer solubility but the former was measured in more rapidly quenched samples. The distribution coefficient is 8×10^{-6}. Preferential trapping of electrons by iron centers was shown by Hall mobility measurements on optically-excited charge carriers. Lifetime studies by the photoconductive decay method indicated a larger capture cross section for electrons than for holes.

Copper introduced a donor level at 0.24 ev and an acceptor level at 0.49 ev, both as measured from the valence band. The maximum electrical activity in quenched samples was 5×10^{14} cm^{-3} out of a total concentration of 10^{18} cm^{-3} at 1200°C. Infrared photoconductivity spectra support the position of the deep levels due to iron and copper.

The apparent lack of electrical activity or inconsistency in producing a level is discussed for a number of other elements in silicon. Precipitation while cooling from high temperature is believed to reduce the soluble component of most of these elements below the observable limit of ~10^{14} cm^{-3}.

INTRODUCTION

Single crystal silicon has been doped with iron or copper by using techniques already described for manganese,[1] gold,[2] and zinc[3] in silicon. These elements in silicon are characterized by relatively low distribution coefficients, low solubilities, and high diffusion coefficients as compared to the Column III and V elements. Both iron and copper introduce deep levels into the forbidden band of silicon which are observable by electrical and optical measurements.

IRON-DOPED SILICON[4]

Electrical Measurements

The earliest measurements were made on sections of single crystal silicon grown from melts doped with iron.[5] When iron was added to high purity *p*-type silicon, the concentration of holes was reduced by as much as 3×10^{14} cm^{-3} indicating that iron acted as a donor impurity. The distribution coefficient was determined from electrical measurements to be between 5×10^{-6} and 10×10^{-6} in a series of crystals whose initial acceptor concentrations ranged from 5×10^{13} to 2×10^{14} cm^{-3}. The use of radioactive iron-59 as a tracer gave a distribution coefficient of 6×10^{-6}. Each iron atom appeared capable of giving up one electron.

Concentrations of iron greater than 10^{15} cm^{-3} but less than 10^{16} cm^{-3} were obtained by diffusing iron into *p*-type silicon overnight at 1200°C in sealed quartz tubes and quenching in water. Most of the iron in these samples was electrically inactive as was demonstrated by removing the samples from their tubes and, after measurement, inserting them into the 1200°C furnace again under argon atmosphere. After about an hour, the samples were fast-quenched by blowing into ethylene glycol. Up to 1.5×10^{16} cm^{-3} donors were then observed. In all cases, when the iron concentration exceeded the acceptor concentration, the temperature dependence of resistivity ρ and Hall coefficient R_H indicated an ionization energy of 0.40 ev, as shown in Fig. 1.

When iron was added to an *n*-type melt or diffused into *n*-type silicon at high temperatures and quenched, no changes in ρ or R_H were observed. Thus there does not appear to be an acceptor level for iron, at least at concentrations of 10^{14} cm^{-3}.

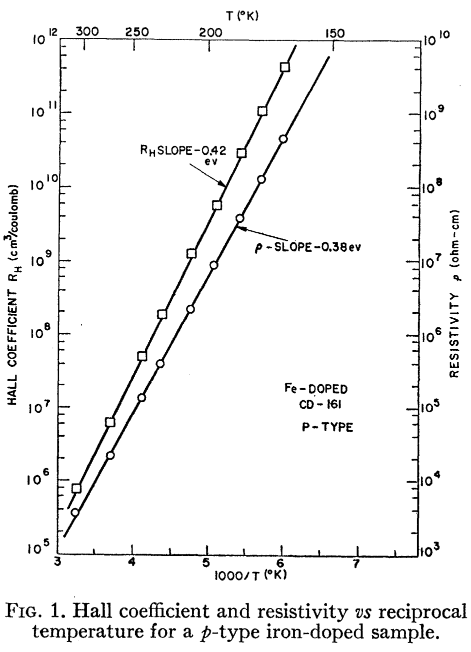

Fig. 1. Hall coefficient and resistivity *vs* reciprocal temperature for a *p*-type iron-doped sample.

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[1] R. O. Carlson, Phys. Rev. **104**, 937 (1956).

[2] Collins, Carlson, and Gallagher, Phys. Rev. **105**, 1168 (1957).

[3] R. O. Carlson, Phys. Rev. **108**, 1390 (1957), this issue.

[4] A preliminary report of this work was given by C. B. Collins, Bull. Am. Phys. Soc. Ser II, **1**, 48 (1956).

[5] For crystal doping, the iron purity was of critical importance. We are indebted to G. A. Moore of the National Bureau of Standards for supplying us with some high-purity iron as described by G. A. Moore [Trans. Am. Inst. Mining Met. Engrs. **197**, 443 (1954)].

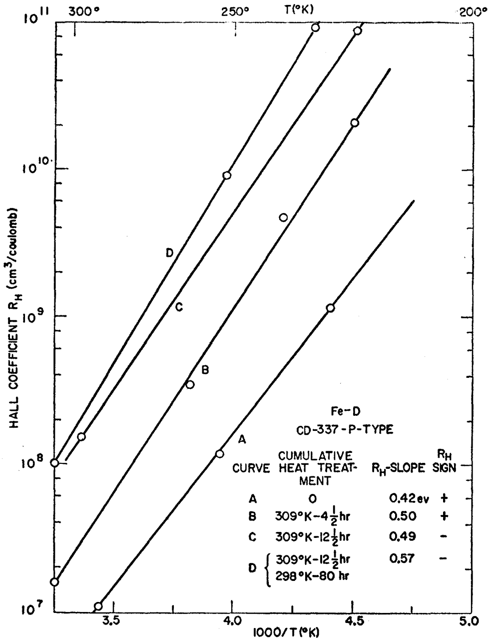

FIG. 2. Heat treatment of *p*-type iron-doped sample. The energy level positions are ~0.02 ev less than the R_H-slope values to correct for the $T^{\frac{3}{2}}$ dependence of density of states near the valence or conduction band edges.

Changes take place in iron-doped silicon which cause a conversion in ionization energy from 0.40 to 0.55 ev. This conversion occurs in the order of a month at room temperature but speeds up to about 5 hours at 50°C. Figure 2 shows part of a sequence of heat-treatment studies on a sample with an initial acceptor concentration of 1×10^{15} cm^{-3}. After the iron diffusion at 1200°C for 65 hours and the rapid-quench procedure, the 0.40-ev level was observed. The R_H slope in Fig. 2 increased in the course of heating at only ~10° over normal room temperature, converting in sign and ending up after a weekend at room temperature close to a 0.55-ev slope. On the basis of the room temperature mobility, this level is measured from the conduction band edge rather than from the valence band edge. Further heating of this sample (not shown) at 86°C caused partial return to its original type and resistivity.

Other *p*-type samples have been cycled between the 0.40-ev and the 0.55-ev level by appropriate heat treatment. Treatment at temperature to ~70°C causes conversion to the upper level; in the range ~70°C to ~200°C the conversion is towards the lower level. Heating above these temperatures for more than a few minutes results in irreversible loss of the iron as far as observable electrical effects are concerned. Probably the iron has precipitated in the volume or at the sample surfaces.[6]

Speculation as to the donor or acceptor nature of the 0.55-ev level led to experiments to determine whether the net residual acceptor concentration could be changed by ion pairing of $Fe^{+}-B^{-}$ as was found by Reiss *et al.*[7] for $Li^{+}B^{-}$. Samples were maintained at 400°C for 65 hours to give the iron an opportunity to diffuse to the boron. One control sample was immersed in a tin bath, a second sample was immersed in a tin bath saturated with iron, and a third sample which had been saturated with iron at 1200°C was heated without tin. The Hall coefficient was measured to liquid hydrogen temperature for all three samples, but no significant changes in acceptor concentrations could be detected from the temperature behavior. Therefore no ion pairing was observed. If one assumes that ion pairing does not occur at room temperature and that the net residual acceptor concentration remains constant, then the 0.55-ev level must be a donor level arising from iron centers with greater than 10^{15} cm^{-3} concentration. The nature of the conversion from one donor level to the other is not understood.

Optical Measurements

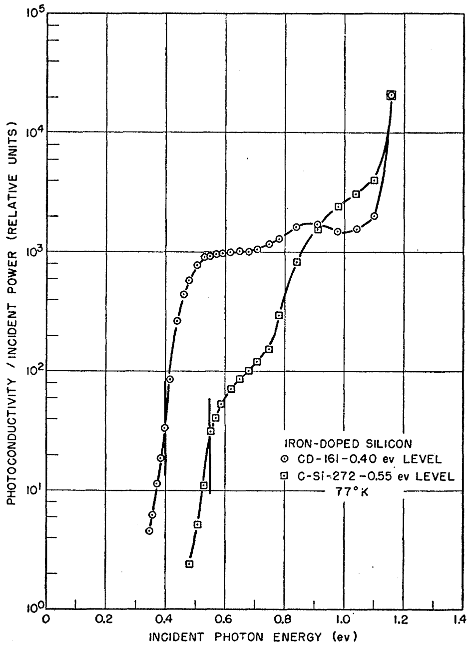

FIG. 3. Photoconductivity spectra of iron-doped silicon samples with thermal ionization energies shown for comparison. Curves were shifted to overlap at 1.16-ev photon energy.

The spectra of impurity photoconductivity shown in Fig. 3 were measured by Newman on silicon domin-

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[6] C. J. Gallagher [Phys. Rev. **100**, 1259(A) (1955)] observed a 0.40-ev level in some undoped *p*-type silicon samples on fast quenching from temperatures between 800°C and 1350°C. The level converted to a 0.55-ev level on standing at room temperature. At 200°C, his samples converted back to their original resistivities in two hours. This behavior, very similar to that of iron-doped silicon samples, could not be reproduced in all *p*-type silicon. Care was taken to insure that iron was not introduced into a sample during handling prior to the quenching. Whether iron was already present in some silicon as the cause of the 0.40-ev level could not be established. For all the silicon used in the present experiments, control runs were made to establish that no change in resistivity occurred on quenching unless the samples were deliberately doped.

[7] Reiss, Fuller, and Morin, Bell System Tech. J. **35**, 535 (1956).

ated by the iron 0.40-ev and 0.55-ev levels. The techniques used have been described.[8] For the p-type sample there is reasonable agreement between the optical and thermal ionization energies. For the n-type the optical ionization energy for exciting electrons out of the upper level approximates the 0.55-ev value of electrical measurements; in addition the inflection at ~0.8 ev may be due to excitation of electrons out of the 0.40-ev level to the conduction band.

The Hall mobility of optically-excited charge carriers was studied for the same p-type iron-doped sample, CD-161, for which thermal and optical ionization energies were shown in Fig. 3. Charge carriers were excited by light from a tungsten lamp which was passed through either a silicon or a germanium filter maintained at 77°K. Radiation passing through the silicon filter has a spectral distribution such that the dominant effect is the excitation of holes and electrons from the silicon lattice rather than from impurity centers. Radiation through the germanium filter can excite charge carriers only from the impurity centers. Figure 4 shows the Hall mobility as a function of conductivity at 156°K for these two cases. The lower curve obtained with extrinsic radiation shows no change in the mobility of holes over four decades change in conductivity. The upper curve, obtained with mixed intrinsic and extrinsic radiation whose predominant effect is to excite holes and electrons from the silicon lattice, shows only hole conductivity[9] at essentially constant mobility over nearly five decades change in conductivity. This is a case of preferential electron trapping, similar to the behavior of manganese sites in silicon.[1]

Small concentrations of iron in silicon have a deleterious effect on the lifetime of minority carriers as shown in Fig. 5. The three crystals for which lifetime are shown were grown from the same starting material, the first crystal C-Si-283 being undoped, the other two having iron added as shown. At the doping point, the iron concentrations in the two crystals are $\sim 5\times10^{12}$ cm^{-3}. Measurements by G. W. Ludwig showed the 50-microsecond lifetime of holes in n-type crystal C-Si-288 to be independent of temperature over a range from 250° to 350°K. The calculated recombination cross section for holes, A_p, is 3×10^{-16} cm^2. Similar measurements by W. W. Tyler on p-type iron-doped crystal C-Si-286 showed an increase in electron lifetime above room temperature and evidence of a 30-millisecond trap at 250°K. The recombination cross section for electrons, A_n, is greater than 15×10^{-16} cm^2 since it has not been shown to be independent of temperature. These cross sections are the order of atomic dimensions just as Burton *et al.*[10] found for copper and nickel in germanium. For iron in silicon, $A_n > A_p$; whereas for copper and nickel in germanium, $A_p > A_n$.

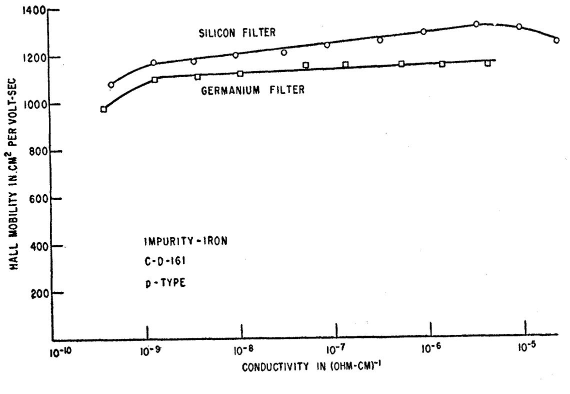

FIG. 4. Hall mobility of optically-excited carriers in a p-type iron-doped sample with the 0.40-ev level. Sample temperature 156°K.

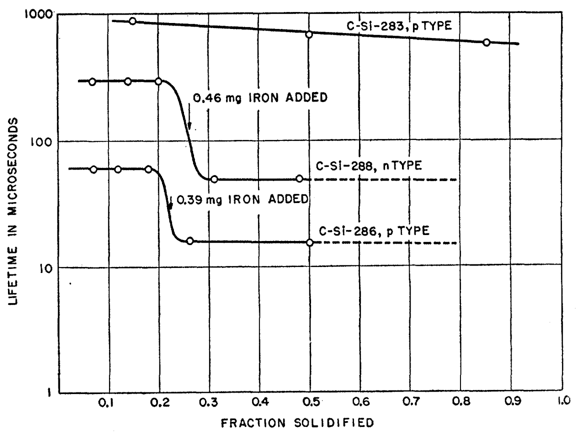

FIG. 5. Effect of iron on lifetime of minority carriers. The silicon crystals weighed about 20 g.

Diffusion and Solubility Studies

The solubility of iron in silicon was measured by diffusing it into p-type samples with 4×10^{16} cm^{-3} net acceptor concentration. In three doped samples quenched rapidly from 1200°C, the change in resistivity corresponded to $(1.3\pm0.5)\times10^{16}$ cm^{-3} added donors while a control sample similarly quenched showed the same resistivity as the original silicon. This solubility is three times the solubility measured by Struthers[11] at 1200°C using radioactive iron-59. Our experiments with iron-59 confirmed Struther's data at 1200°C, but the saturated radioactive samples could not be quenched rapidly because of their larger size. As an additional factor, the amount or iron in sealed tubes for the radiotracer experiments did not exceed 0.03 mg while

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[8] R. Newman, Phys. Rev. **99**, 465 (1955).

[9] The Hall coefficient $R_H = -(nb^2-p)/e(nb+p)^2$, where n and p are the free electron and hole concentrations, respectively, b is the electron to hole mobility and is approximately 4 for silicon, e = absolute value of the electronic charge. R_H should reverse sign as $n \rightarrow b$.

[10] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

[11] J. D. Struthers, J. Appl. Phys. **27**, 1560 (1956).

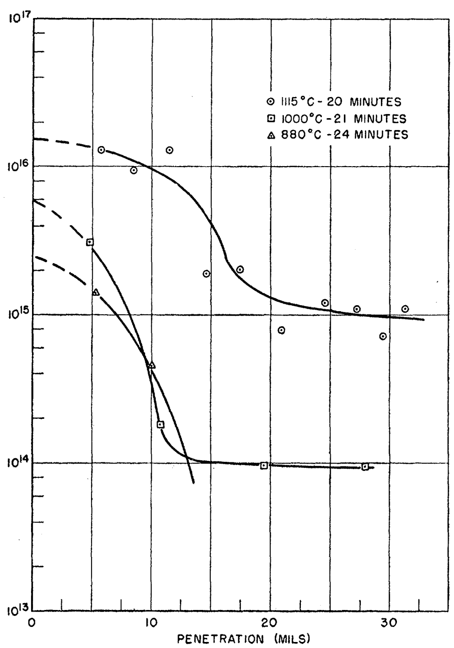

FIG. 6. Penetration curves of radioactive iron-59. The curves for 1000° and 1115°C suggest two diffusing species.

for the conductivity samples the usual amount of iron present was one to five mg.[12]

Diffusion experiments indicated that two species of iron might be present. These experiments were carried out on silicon samples coated with radioactive iron chloride. The samples were not in sealed tubes but were placed in a furnace under an argon atmosphere and quenched rapidly by dropping into ethylene glycol. Figure 6 shows the data for diffusions carried out at 880°, 1000°, and 1115°C for times close to 20 minutes. Extrapolation of the shallow penetration data back to the surface gives the approximate solubility of a more slowly diffusing species. The plateaus in the curves for 1000° and 1115°C measure the solubility of a faster diffusing species; the measurements for 880°C could not be made below $\sim 8\times10^{13}$ cm^{-3} because of the low radioactivity. These solubilities are plotted in Fig. 7 along with the concentration of electrically active iron observed in saturated samples after fast quench from 1200°C. The curve of Struthers,[11] given by the solid line, is reasonably fitted by the solubilities of the faster diffusing species. This diffusion of iron into silicon is suggestive of the mechanism by which copper diffuses into germanium.[13] Copper diffuses rapidly interstitially and converts to substitutional copper at diffusing vacancy sites. Substitutional copper itself diffuses very slowly, but the apparent diffusion is determined by the vacancy generation rate and the latter by the dislocation density. Our study of iron diffusion was made in crucible-grown, slowly rotated silicon.

Diffusion coefficients from the Fig. 6 data are greater than 5×10^{-6} cm^2/sec at 1000° and 1115°C for the faster diffusing species (greater than Struthers values[11]). The slower diffusing species varies from $\sim 7\times10^{-7}$ at 1115° to 1.3×10^{-7} at 880°C.

COPPER-DOPED SILICON

Electrical Measurements

When copper was diffused into silicon at 1200°C, up to 5×10^{14} cm^{-3} change in carrier concentration was observed in both n- and p-type silicon of $\sim 10^{15}$ cm^{-3} initial concentration.[14] Variation of diffusion temperature or time or of the quenching rate did not increase the electrically active concentration of copper. When the initial donor concentration was less than 5×10^{14} cm^{-3}, the sample converted to p-type and resistivity and Hall effect measurements revealed an acceptor level at 0.49 ev. With the initial acceptor concentration less than 5×10^{14} cm^{-3}, the sample remained p type and showed a donor level at 0.24 ev. Figure 8 shows typical Hall effect measurements which revealed these two

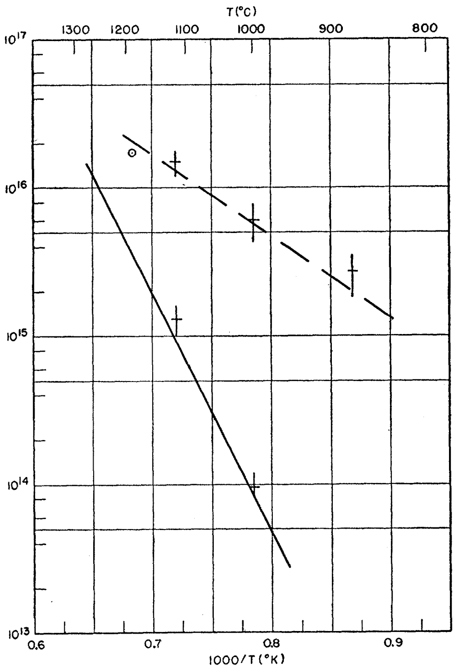

FIG. 7. Solubilities of the two diffusing species of iron derived from Fig. 6. The solid line represents the curve of Struthers in reference 10. The circled point is derived from electrical measurements in p-type silicon assuming one electron available per iron atom.

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[12] In radiotracer studies of zinc solubility in silicon, it was found that the amount of zinc in the tube had to exceed greatly the amount required to saturate the sample in order to attain maximum solubility. See reference 3.

[13] A. G. Tweet and C. J. Gallagher, Phys. Rev. **103**, 828 (1956); C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **28**, 40 (1957); F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

[14] An indication that copper acted as an acceptor was given by C. S. Fuller and J. D. Struthers [Phys. Rev. **87**, 526 (1952)].

levels. A number of other levels within the forbidden band (~0.23 ev from the conduction band and 0.45 ev from the valence band) were observed after heat-treating and quenching copper-doped silicon samples. These levels were not reproducible, however, and may be due to impurities present in the copper itself. No search was made for a possible double acceptor level in view of the low and uncontrollable solubility of copper.

Optical Measurements

The photoconductive spectra measured by Newman is shown in Fig. 9. There is good agreement between the thermal and optical ionization for the 0.24-ev level; it is difficult to interpret the curve for the sample with the 0.49-ev level.

Copper acts to reduce lifetime in doped crystals. However, no quantitative experiments were carried out because the precipitation process makes it difficult to ascertain the concentration of soluble copper in doped crystals.

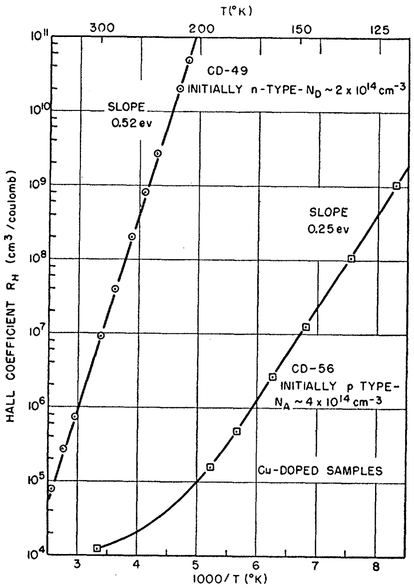

FIG. 8. Hall coefficient *vs* inverse temperature for an *n*- and a *p*-type silicon sample into which copper was diffused at 1200°C. Both samples are now *p* type.

Diffusion and Solubility Studies

The solubilities as determined with the use of radioactive copper-64 were in general consistent with data of Struthers.[11] Since the total copper solubility at 1200°C is ~10^{18} cm^{-3}, it follows that less than one atom out of a thousand remains in an electrically active state after quenching to room temperature. Evidence that this copper is in the form of precipitates in the bulk of the silicon was given by Dash,[15] using an infrared image tube to "see through" the silicon. Diffusion experiments at 900° to 1050°C gave ~10^{-5} cm²/sec for the diffusion coefficient though most of the penetration curves were not well fitted by the conjugate error function. Other published values[11,16] are 3×10^{-5} and 5×10^{-5} cm²/sec.

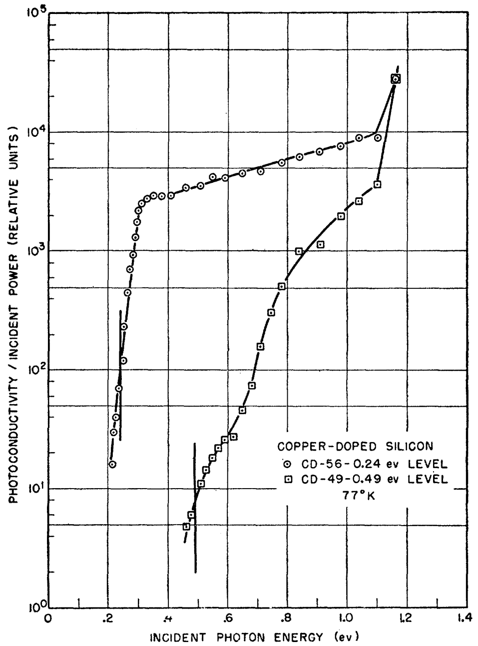

FIG. 9. Photoconductivity spectra of copper-doped silicon samples with thermal ionization energies shown for comparison. Curves were shifted to overlap at 1.16-ev photon energy.

SUMMARY AND DISCUSSION OF DEEP LEVELS

Figure 10 summarizes the deep levels discovered so far in silicon omitting the Column III and V elements and lithium.[17] The zinc levels (except for the 0.55-ev

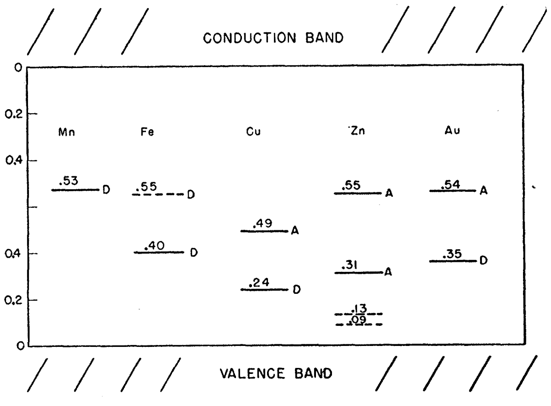

FIG. 10. Deep energy levels in silicon. Summary of all published work to date. See text for references.

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[15] W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).

[16] Fuller, Struthers, Ditzenberger, and Wolfstern, Phys. Rev. **93**, 1182 (1954).

[17] These elements have relatively shallow levels, except for In at 0.16 ev and Tl at 0.26 ev from the valence band, and are tabulated by H. Brooks, in *Advances in Electronics and Electron*

level) were described by Fuller and Morin.[18] They attributed a complex of shallower levels (0.13, 0.09, 0.08 ev) to ion-pairing of zinc with the Column III acceptor present. The elements in Fig. 10 each have one donor state with the possible exception of zinc. The coincidence of levels at ∼0.55 ev from the conduction band cannot arise from a common impurity. The manganese level is observed only when added to *p*-type silicon, the gold level only when added to *n*-type silicon. Hence the former is a donor, the latter an acceptor. The solubility of the four elements in silicon, as measured by the electrical activity of the 0.55-ev levels, is different for each element. Also, on heat treatment, the levels have different degrees of stability.

The scarcity of deep acceptor levels in silicon is in marked contrast to the behavior of these elements in germanium, where iron, manganese, and zinc have two acceptor states each[19] while copper and gold have three acceptors each.[20] The tendency to complete tetrahedral bonds is clear in germanium whereas donor states are lacking except for the Column V elements, tellurium[21] and gold.[22] The two levels of gold and the acceptor levels of zinc and copper are shifted upwards in the forbidden band of silicon as compared to the levels of these elements in germanium. A study of the levels of gold and copper in germanium-silicon alloys[23] may reveal the intermediate stages in the transition of the level pattern of an element in germanium to that in silicon.

The presence of levels near the middle of the band gap suggests that one or more of the elements in Fig. 10 may be responsible for the recombination center observed in lifetime studies of junction diodes and reported by Pell and Roe[24] as ∼0.5 ev deep. Haynes and Hornbeck[25] observed in *p*-type silicon electron-trapping levels at 0.57 and 0.79 ev from the conduction band. These levels were found in "as grown" crystals and they could not introduce these traps by adding chemical impurities, by bombardment with high-energy particles, or by bending, twisting, or compressing the silicon. The electron trapping which we have produced by manganese or iron doping bears some similarity to these traps but further experiments would be required to determine whether there is a real correlation.

We studied the effect of a number of other elements in silicon. In some cases (Co, Mg, Ni, Te), there was no electrical activity in 100-ohm-cm *n*- or *p*-type silicon. Thus less than 10^{14} cm^{-3} ionizable centers were available from these elements. Radiotracer studies with cobalt-60 revealed the solubility to be 1×10^{16} cm^{-3} at 1200°C; in a doped crystal the distribution coefficient was 8×10^{-6}. These values are almost identical with those for iron which has readily observable activity. Radiotracer experiments carried out with Cr and Se indicated that their solubilities were $<10^{15}$ cm^{-3} at 1200°C (or their diffusion coefficients $<10^{-8}$ cm^2/sec). For Ag, Cd, and Pd, the electrical activity was marginal, some samples having a level, others no level, while the radiotracer solubility was 10^{15} to 3×10^{16} cm^{-3} at 1200°C. Pt also gave rise to levels but not reproducibly. This lack of electrical activity is due mostly to precipitation of the elements during their quenchs from high temperature. Dash[26] found direct evidence of precipitates by the infrared snooperscope technique[15] in silicon crystals doped with Ag, Cu, Co, Fe, Mn, Ni, U, and Zn. Further study of elements in silicon will require the availability of purer silicon with ∼10^{13} cm^{-3} net impurities which does not heat-treat at high temperature, and faster quenching cycles to keep the precipitation to a minimum.†

ACKNOWLEDGMENTS

The authors wish to thank G. W. Ludwig and W. W. Tyler for many of the lifetime measurements, and R. Newman for the infrared studies. Sample preparation and cryostat measurements were carried out by R. Holcomb, G. Brower, R. Thomas, and J. Sobieski.

Physics, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 110 and N. B. Hannay, in *Progress in Semiconductors* (Heywood and Company, Ltd., London, 1956), Vol. 1, p. 18.

[18] C. S. Fuller and F. J. Morin, Phys. Rev. **105**, 379 (1957).

[19] W. W. Tyler and H. H. Woodbury, Phys, Rev. **102**, 647 (1956).

[20] H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

[21] Armstrong, Tyler, and Woodbury, Bull. Am. Phys. Soc. Ser II, **2**, 265 (1957).

[22] W. C. Dunlap, Jr., Phys. Rev. **100**, 1629 (1955).

[23] M. L. Schultz, Bull. Am. Phys. Soc. Ser II, **2**, 135 (1957).

[24] E. M. Pell and G. M. Roe, J. Appl. Phys. **27**, 768 (1956).

[25] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **100**, 609 (1955); J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).

[26] W. C. Dash (private communication).

† *Note added in proof.*—The possible interaction of impurities with oxygen, present in varying amounts in all silicon, was not studied. The silicon used for our deep level studies came from crystals grown in crucibles under conditions of slow or zero rotation.

M. Tannenbaum and H. Bridgers of the Bell Telephone Laboratories reported the observation of the two levels of copper in silicon in a paper presented at the October, 1956, meeting of the Electrochemical Society in Cleveland.