Progress in Semiconductors

1

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PREFACE

AT the present time about a thousand papers are published each year on semiconductors or closely allied subjects. Of these, the specialist in the field should, if possible, give careful study to several hundred. If, having done this, he has any time available to contribute new knowledge himself, he is a man of exceptional ability. In reality the result is even more intensive specialization with the chemist, the metallurgist, the physicist, the mathematician and the electrical engineer knowing each year less and less of the others' problems and achievements. The situation is aggravated, too, by the necessity for numerically large teams which encourages extreme specialization.

The critical review article is now the accepted means of overcoming these difficulties by giving the busy man a quick survey of the field. It has been noticed, however, that a flood of review articles frequently indicates that the subject under study is quietly dying on its feet, which is certainly not true of semiconductors. Indeed, review articles in this field are comparatively rare. Our publishers, my co-editors and I felt, therefore, that an annual book, containing a number of review articles written by leading specialists in the field, could serve a useful purpose. In view of the rapid growth of the subject, any article could be expected to be out of date in a few years, and this consideration, together with the wide field to be covered, dictated the necessity for annual publication.

We shall cover all aspects of semiconductors including, at least to a limited extent, applications of semiconductor devices. We hope to include articles of interest both to the specialist in the field and to those working on allied fields. Thus, for example, the paper by Garreta and Grosvalet on the PME effect includes a significant amount of original work and is primarily of interest to the specialist. On the other hand, Dr. Evans's paper on high-frequency transistors should be of interest to the circuit designer and give him some indication of the problems to be faced in meeting his requirements. In addition, there is the sweeping and invaluable review of a large field, well represented by Dr. Hannay's paper on silicon.

To many workers in the field the words semiconductor research are synonymous with transistor research. We do not intend to be so restrictive. Nevertheless, work on germanium and silicon must inevitably occupy most of our pages: they are probably the most studied and best understood elements in the periodic table. The transistor, too, is by far the most important single device based on semiconductors. Indeed, it can be argued that serious progress in the field of semiconductors dates from the discovery of minority carrier injection and the development of zone refining, both at the Bell Telephone Laboratories. I have heard work prior to 1948 dismissed as 'pretransistential'. I believe, however, that we must not forget other important aspects of semiconductor research, such as luminescence, the photographic process and photoconductivity. This type of paper is well represented by that of Prof. Garlick.

Finally I should like to draw attention to the international flavour of this volume. My co-editors and I have the whole world, this side of the Iron Curtain, to call upon, and it is intended to draw contributions for succeeding volumes from every available source, wherever semiconductor research is being carried out.

A. F. GIBSON.

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RECENT ADVANCES IN SILICON

1. INTRODUCTION

Silicon is a semiconductor that promises to be of great practical importance, principally because its energy gap of 1·10 eV. leads to two very important consequences. Firstly, the material becomes intrinsic at much higher temperatures ($>$ 200° C.) than does germanium, so silicon devices will be operative under temperature ambients well in excess of those at which germanium devices are no longer usable. Secondly, the larger energy gap in silicon results in lower reverse currents for P–N junctions than are the case for germanium. These currents for silicon are three orders of magnitude less than for germanium. This property is of great importance in many circuit applications.

The purification of silicon is more difficult, however, than is the purification of germanium. This is because of its higher melting point, its high reactivity when molten, and because of unfavorable distribution coefficients for certain impurities. Only recently has it been possible to purify silicon to the same degree as germanium. The intrinsic carrier concentrations of silicon at room temperature are less than 10^{10} cm^{-3}, corresponding to an intrinsic resistivity at 300° K. of 230,000 Ωcm. This means that in order to obtain intrinsic silicon, electrically significant impurities would have to be reduced to a concentration of less than 10^{10} cm^{-3}, which is three orders of magnitude lower than the corresponding maximum impurity concentration necessary to obtain intrinsic germanium. The best silicon that has been prepared to date is about two orders of magnitude less pure than that required for intrinsic behavior. Steady progress has been made in the purification of silicon, however, and it is not unreasonable to expect that the preparation of single-crystal intrinsic silicon may be feasible. Lifetimes in silicon have also been found to be high, crystals having been grown with lifetimes in excess of 1 msec., so that in this respect also silicon compares favorably with germanium. On the other side of the picture, however, carrier mobilities in silicon are one-third to one-half those for germanium, and other factors being equal this will generally result in poorer frequency limits for silicon devices.

This article will review the present state of silicon—its purification and preparation, the understanding of its properties, and the state of development of silicon devices. No pretense is made that the material described is completely comprehensive. Much of the work that has been done in the last year or two is mentioned, however, and the bibliography includes references to most of the recent work. Of necessity, only brief mention is made of many interesting investigations. Of the material described in more detail, we have chosen arbitrarily to draw rather heavily on some of the work carried out recently by several of our colleagues at the Bell Telephone Laboratories.

2. SILICON PREPARATION

2.1. **Preparation of High-purity Polycrystalline Silicon**

There are a number of methods that have been used for the preparation of raw

silicon of high purity. Some of these methods have been discussed in a recent review by Lyon[1], who gives references to much of the earlier work, by Theuerer[2], and by von Wartenberg[3]. Ordinary commercial silicon is prepared in an electric arc furnace, with silicon dioxide (sand) being reduced by carbon electrodes. This process can produce silicon that is about 97 per cent pure. If silicon of this purity is acid leached, it may be purified further, to about 99·8 per cent. Fusion of silicon of this quality, with the addition of controlled impurities and with controlled directional solidification, produces material which is satisfactory for the production of point-contact diodes that are extremely useful for radar and other microwave applications[4]. Such material, however, is not of sufficient purity to be of much interest in most semiconductor applications. Furthermore, because several elements (notably boron) have unfavorable distribution coefficients in silicon, the zone refining process which has been so useful for the purification of germanium[5] cannot be used as efficiently to accomplish much purification of this type of silicon. Accordingly, other methods of purification of the material have been investigated. These methods, in general, involve the preparation of a volatile silicon compound such as the hydride or one of the halides. This volatile compound is purified by fractional distillation or by some suitable chemical method, and is then reduced to produce the final high-purity silicon. A number of these reduction methods have been described in literature.

Stock and Somieski[6] have discussed the thermal decomposition of silanes, and further work using this method has been carried out recently by several laboratories.

The hydrogen reduction of silicon tetrachloride has been discussed by a number of authors[2, 7, 8]. In this method, silicon tetrachloride that has been purified by fractional distillation is reduced on a hot surface, in the presence of hydrogen gas. Theuerer[2] has described an apparatus using this method, in which the silicon is deposited on a tantalum tape. Purities of the order of 1 part in 10^9 are achieved, with the principal residual impurities being boron and phosphorus. This purity level corresponds to resistivities of approximately 100 Ωcm. The further purification of this material, resulting from zone refining in the course of preparation of single-crystal material, will be described in the next section.

The principal method that has been used commercially to prepare high-purity silicon is the reduction of silicon tetrachloride by zinc vapor. This method, which is the basis for the du Pont silicon process, has been discussed by Lyon *et al.*[9] Fractionally distilled silicon tetrachloride and zinc vapor of high purity are injected into a fused silica reactor at 950° C. Operated as a batch process, approximately 15 lb. of silicon is obtained in each run. The purities of the silicon obtained by this process are not quite as high as those obtained in the hydrogen reduction process, and it contains substantial amounts of zinc as a contaminant. The zinc is easily removed, however, in any subsequent fusion of the silicon, because of its high vapor pressure.

Silicon tetraiodide has also been used as a starting material for the reduction process. Litton and Anderson[10] have recently described the preparation of silicon by the thermal decomposition of the iodide in a de Boer iodide cell. By using a modified iodide process in which the fractionally distilled iodide was thermally decomposed in an intermittent flow system, they were able to prepare P-type silicon of 30–200 Ωcm.

2.2. Crystal Growing; Zone Refining

Various methods have been employed to obtain single crystals from high-purity polycrystalline silicon. For example, attempts have been made to grow crystals from molten alloy phases; in particular from aluminum, silver and zinc[9], gallium and indium[11], tin[12], and from gold[13]. The material produced in this way is in general less pure than that obtained in other ways, and the preparation of single crystals of reasonable size is usually difficult. Consequently, these methods have been largely experimental.

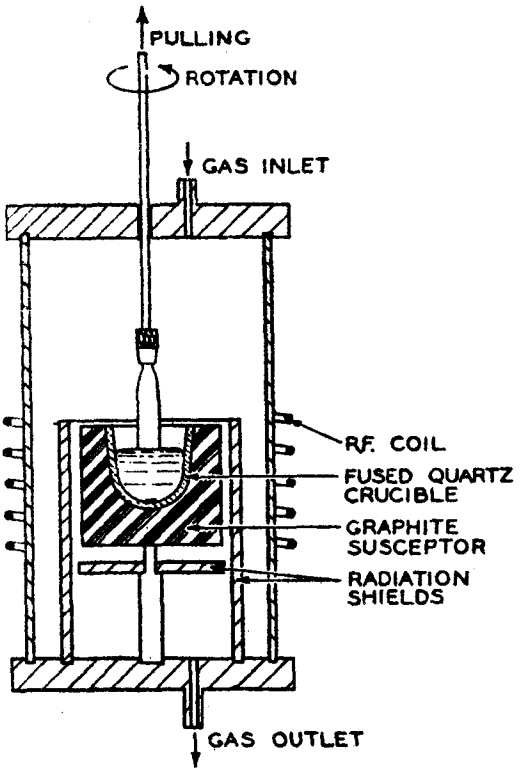

Figure 1. *Apparatus for pulling single-crystal silicon.* (*Buehler*)

The most widely used method is the crystal-pulling method of Teal, Little and Beuhler[14, 15] (see also [16]). Although the technique is basically similar to that usually used for germanium, the higher melting point of silicon makes necessary a modification of the crucible system used. A number of crucible materials have been tried for silicon, with varying degrees of success; the most generally satisfactory has been found to be fused quartz. A typical crystal-pulling apparatus is shown in Figure 1, which shows the basic similarity to germanium crystal-pullers. In the apparatus shown in Figure 1, heating is by R.F. induction heating, with approximately a 10 kW. R.F. induction heater being required for an apparatus

capable of producing crystals of 50–100 g. size. A graphite susceptor for coupling in the R.F. power is used, with a fused quartz liner to contain the silicon. This structure is supported on appropriate graphite rods and is surrounded by a radiation shield. A quartz envelope permits control of the atmosphere, so that an inert gas can be passed over the silicon while the crystal is being grown. The temperature control is obtained by regulating the R.F. power input so that the temperature of the graphite susceptor, as measured by a thermocouple, remains constant to within 0·1° C. The arrangements for inserting a single crystal seed and the mechanism for pulling and rotating of the seed during the growth are similar to those conventionally used for germanium. In a later section some interesting consequences of growing crystals without rotation will be discussed.

Many variations of this apparatus have been used successfully. Different heating arrangements can be used; for example, resistance heaters of an appropriate material, such as graphite, avoid the necessity for the R.F. induction unit. Many different sizes and shapes of crucibles can be used, and in some cases geometries for the elimination of graphite from the system, or for the isolation of radiation shields, heaters, *etc.* from the silicon, have been incorporated. Single crystals are easily grown by the pulling technique, and they range in size from 5 g. up to 125 g. or more. Crystals may be grown in any of several orientations, the most commonly used being the [100] and [111] directions. Figure 2 shows three examples of crystals grown by the pulling technique in an apparatus similar to that shown in Figure 1, showing various sizes and shapes. Manual control of the pulling rate and of the setting of the temperature control system is sufficient to keep the diameter reasonably constant, although programming can be used when it is desirable to have a better diameter control. Doping of the crystals can be accomplished with any of the Group III or Group V elements by injecting either the pure element or a piece of heavily doped silicon into the melt during growth. The most volatile of these elements, phosphorus and arsenic, are partially lost from the melt during growth; nevertheless, reproducible results are obtainable using these as doping agents. In doping with aluminum, oxidation must be avoided, as silicon will not reduce the oxide. In the case of boron it will, however, and no difficulties are encountered. The growth rates necessary to obtain single crystals range from about 10^{-3} cm.sec^{-1} to a maximum of about 10^{-2} cm.sec^{-1}. Random fluctuations in the growth rate are of the order of 10^{-3} cm.sec^{-1}, so that any attempts to pull at lower rates than this are impractical. These random fluctuations originate from such causes as thermal asymmetry of the melt, the chemical reaction between the molten silicon and the fused quartz crucible, and non-uniform wetting of the crucible, which results in 'hang-up' or mechanical asymmetry of the melt.

The reaction $Si + SiO_2 \rightleftarrows 2SiO$ proceeds continuously during the growth of a crystal because the silicon monoxide produced is quite volatile at 1414° C. In the growth of a typical crystal, something of the order of 50 mg. of fused quartz reacts in this way. Hence, any appreciable concentration of impurities in the quartz will introduce impurities into the silicon melt. Because of the unfavorable distribution coefficients of certain impurities in silicon (see section 3), the most notable of which is boron with $k \sim 0{\cdot}9$, when such elements are present as impurities in the quartz the resulting contamination of the melt will also result

in contamination of the silicon crystal. The degree to which this occurs has been investigated in a series of experiments by Buehler and Maita[17] at Bell Telephone Laboratories in which approximately fifteen crystals were grown, each from a new fused quartz crucible. The crystals were analyzed by low-temperature Hall effect (see sub-section 5.1) to determine donor and acceptor concentrations, and it was found that the contamination from the quartz crucible during the growth of a crystal amounted to less than 5×10^{13} cm^{-3} in all cases, corresponding to P-type resistivities of approximately 300 Ωcm. It is not certain as yet what level of impurities any actual contamination may result in.

Two methods of applying Pfann's[5] zone-refining technique have been used for silicon. These are zone-refining in a boat and the so-called 'crucibleless' zone-refining. Silicon can be zone-refined in fused quartz boats; methods for doing this have been developed by Horn[18]. This method of zone-refining has not yet been adopted as widely for silicon as for germanium because of the possible danger of contamination from the fused quartz, but it is clearly advantageous for many problems. The apparatus for this type of zone-refining needs little elaboration. R.F. induction heating may be used to heat the silicon directly. The silicon is contained in a thin-walled fused quartz boat in Horn's method, thin walls being necessary to avoid the cracking of the silicon that would occur if thick-walled fused quartz were employed. The fused quartz boat may be contained inside another quartz tube to provide control of the gas atmosphere. Since the silicon cannot usually be heated directly from room temperature by R.F. induction heating at 450 kc/s., which is the frequency of most commercial induction heaters, pre-heating of the silicon in a furnace or by a gas torch is usually necessary in order to increase the silicon conductivity to the point where the R.F. induction heating can become effective.

Another method that has been used for zone-refining is the crucibleless zone-refining, or 'floating zone' method, which has been described by Keck, Emeis, Müller, and others[19–26]. In this method the silicon rod is vertical, and is held rigidly at both ends. The molten zone is supported by surface tension forces, which limit the size of the rod that can be refined by this method to approximately 1 cm. diameter. One molten zone at a time is passed through the silicon rod. Figure 3 shows a schematic of the apparatus that has been used at the Bell Laboratories by Theuerer[2] and Whelan. In this apparatus, the silicon is heated directly by a single-turn R.F. induction coil operating at 5 Mc/s. frequency. This frequency is used to provide greater stability of the molten zone than can be obtained at 450 kc/s. The silicon rod is cemented at both ends to silica support rods and a fused quartz envelope is used to control the gas atmosphere. The whole apparatus can be lowered through the R.F. coil in order to move the molten zone through the rod. The advantage of this method, of course, is that there is no contact of the molten silicon with any crucible material. Single crystals can be grown by seeding the rod with a single crystal at one end. In order to produce single crystals, the zone must move at a rate no greater than about 10^{-2} cm.sec^{-1}. For the preliminary zone-refining passes, somewhat faster movement of the zone is possible. Other workers who have used this method have sometimes heated the silicon by the use of a radiation heater inside the quartz envelope and surrounding the silicon rod. This radiation heater may be heated either by resistance heating or by R.F. induction heating. Such methods are less desirable than the

direct heating method, however, because of the danger of contamination of the silicon by the radiation heater.

A number of crystals have been grown by the floating zone method at Bell Laboratories by Theuerer and Whelan, using the apparatus of Figure 3. One of their rods is shown at the bottom of Figure 2; this rod is approximately 1 cm. in

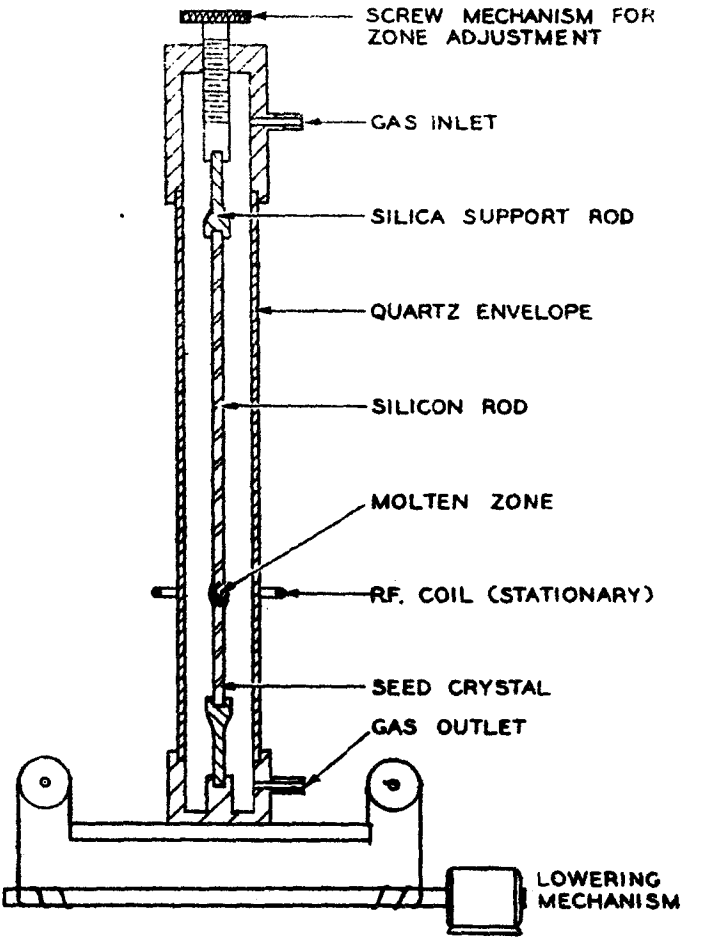

Figure 3. *Apparatus for 'floating zone' method.* (*Theuerer and Whelan*)

diameter, and the single-crystal section is approximately 25 cm. long. Using this method, they have prepared a silicon rod which showed a resistivity of 3000 Ωcm. and a lifetime in excess of 500 μsec. When analyzed by low-temperature Hall effect, this rod was found to have an acceptor concentration $N_{A-} = 4 \times 10^{12}\,\mathrm{cm}^{-3}$ and a donor concentration $N_{D+} = 3 \times 10^{11}\,\mathrm{cm}^{-3}$.

In order to use the floating zone method, one must of course prepare the silicon in the form of a rod of approximately the desired final shape. In the experiments

of Theuerer and Whelan, they have generally used as starting material the hydrogen-reduced silicon described in sub-section 2.1. By sawing the rods lengthwise the tantalum tape used for the deposition may be removed. Several of these half-rods are bundled together and are used as the starting material for the refining. If silicon in the form of a powder is to be used, the material must be prepared in the form of a rod and this can be done by fusion, casting or by sintering. To utilize the floating zone most efficiently and obtain the highest possible purities, it is very important that this preliminary step be performed with the least possible contamination.

3. PHYSICAL CHEMISTRY OF IMPURITIES IN SILICON

A summary of many of the properties associated with impurities in germanium and silicon has recently been given by Burton[27].

3.1. **Distribution Coefficients**

The distribution coefficient, defined as the ratio of the concentration of the impurity in the solid to that in the liquid at equilibrium, has been measured for a number of elements. The values for a number of these, as given by Burton, are shown in Table 1. Two methods have been used for these determinations, radiotracers and conductivity measurements; in the table, the method that was used for the determination is indicated by R or C respectively. The value for iron, which is more recent, has been added to Burton's table.

Table 1 (after Burton[27])

Element	$k = C_S/C_L$	Method	References
B	0·9	C	*a*, *b*
Al	$\geq 0{\cdot}004$	C	*a*, *b*
Ga	0·01	R, C	*c*, *b*
In	5×10^{-4}	R	*c*, *b*
P	0·35	R, C	*c*, *b*
As	0·3	R, C	*c*, *b*
Sb	0·04	R, C	*c*, *b*
Sn	0·02	R	*c*
Cu	4×10^{-4}	R	*d*
Au	3×10^{-5}	R, C	*c*
Ta	1×10^{-7}	R	*c*
Fe	$\sim 1 \times 10^{-5}$	R	*c*

a. N. B. Hannay (unpublished results).
b. Hall. *J. Phys. Chem.* **57**, 836 (1953).
c. J. D. Struthers (private communication).
d. C. D. Thurmond and J. D. Struthers. *J. Phys. Chem.* **57**, 831 (1953).

3.2. **Solubilities**

Very few solid solubilities have been reported for impurities in silicon. Fuller, Thurmond, Struthers and others have reported the solubilities of copper, gold, and lithium[28, 29]. All of these elements show retrograde solubilities with the solubility increasing with temperature to a maximum value and then decreasing with a further increase in temperature. Thurmond and Struthers[28, 30] have

shown that such a behavior is to be expected for impurities of small k, from a consideration of the thermodynamics of dilute solutions, and this is believed to account for the copper and gold solubility behavior. Struthers has also measured the solubilities of iron in silicon over a limited temperature range, finding that the solubility increases sharply over the range 1000–1300° C., from 10^{14} to 5×10^{16} cm^{-3}.

A particularly interesting study of solubility relationships in semiconductors has recently been carried out by Reiss and Fuller[31–34], who have experimentally

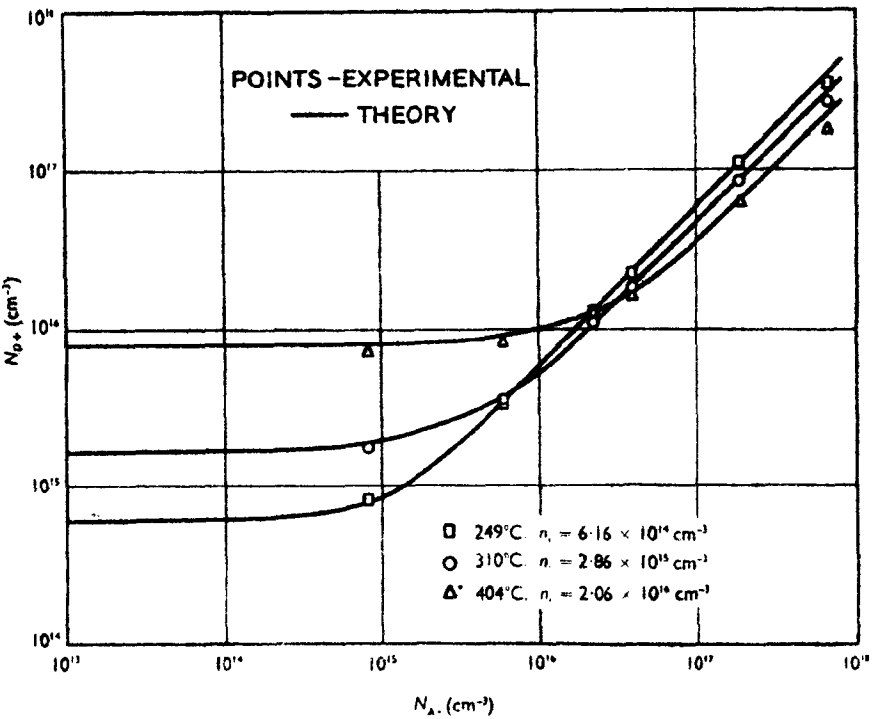

Figure 4. *Solubility of lithium in silicon versus boron concentration, for three temperatures.* (*Reiss and Fuller*[31–34])

[*By courtesy of the American Institute of Mining and Metallurgical Engineers.*

tested these relationships in silicon. Reiss applies the law of mass action, in a manner similar to that familiar in the study of chemical reactions, to the interaction of donors and acceptors in semiconductors, where the following equilibrium holds:

$$\text{hole} + \text{electron} \rightleftarrows \text{recombined pair}$$

The effect of one impurity on the solubility of another will now be considered, and for purposes of illustration the effects of the acceptor boron on the donor lithium will be discussed. The addition of boron to the silicon increases the concentration of holes in the system and drives the above equilibrium to the right, thus reducing the concentration of electrons in the system. This removal of

electrons in turn drives the equilibrium which determines the lithium solubility to the right namely:

$$\text{Li(external phase)} \rightleftarrows \text{Li(in solid solution)} \rightleftarrows \text{Li}^+ + \text{e}$$

The net effect is thus to increase the solubility of lithium in the silicon. By writing the mass action laws for the various equilibria involved, an expression is obtained relating the lithium solubility to its solubility in undoped silicon, the acceptor (boron) concentration, and the intrinsic concentration of holes and electrons in the silicon at the temperature of the experiment. Experiments carried out by Fuller and Reiss have shown quantitative agreement of the experimentally determined solubilities with the theoretically predicted values over several orders of magnitude range in concentration. Some of their experimental results are shown in Figure 4. Their purpose in choosing boron and lithium was to select a system with an immobile acceptor, and with a donor which could be diffused in and brought to its equilibrium solubility rapidly and conveniently. These principles are equally applicable to germanium, and it may be easily seen how they will equally apply in determining the solubilities with any combination of donors and acceptors.

3.3. **Diffusion Coefficients**

Diffusion constants have been measured for several impurities in silicon. Fuller and Ditzenberger[34] find that the diffusion of lithium into silicon follows the law $D = 9{\cdot}4 \times 10^{-3} \exp(-18{,}000/RT)$; at 1000° C., for example, the diffusion coefficient is 10^{-5} cm^{2}sec^{-1}. They have also studied the diffusion of boron and phosphorus[35], both of which follow the approximate law $D = 1 \times 10^{-3} \exp(-58{,}000/RT)$; this corresponds to a value for D of about 10^{-13} cm^{2}sec^{-1} at 1000° C. Dunlap *et al.*[36] gives values for diffusion coefficients at 1100° C., for antimony (10^{-13} cm^{2}sec^{-1}, activation energy 80 kcal.), boron (10^{-12} cm^{2}sec^{-1}, activation energy 80 kcal.) and for gold (10^{-7} cm^{2}sec^{-1}). Struthers[37] has measured diffusion coefficients for copper ($D_{900°} = 5 \times 10^{-5}$ cm^{2}sec^{-1}), gold ($D_{800°} = 5 \times 10^{-8}$, $D_{1000°} = 4 \times 10^{-7}$, $D_{1200°} = 1 \times 10^{-6}$ cm^{2}sec^{-1}), and iron ($D_{1200°} \sim 5 \times 10^{-6}$ cm^{2}sec^{-1}). The Group III and V elements, being substitutional impurities, show very low diffusion coefficients. The much higher values observed for lithium, copper, gold and iron are taken as evidence that they diffuse as interstitial impurities.

The mobility of lithium ions in silicon has also been measured[38, 39]. The lithium has been found to migrate as a single positive charge and it has been shown to follow the Einstein relation, since the diffusion constant calculated from the observed mobility has been found to agree with the measured diffusion constant[39].

4. BULK PROPERTIES OF SILICON

4.1. **Physical Properties**

Various physical properties of silicon have recently been studied. These will be discussed only briefly. Fine[40] has measured the coefficient of linear expansion, the compressibility, and has calculated the specific heat difference ($c_p - c_v$) for silicon. Honig[41] has studied the sublimation of silicon in a mass spectrometer