

# 'DOPING' OF SEMI-CONDUCTORS

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## ABSTRACT

Most of the semi-conductors are formed by addition of foreign substances in an insulator. This is called 'Doping'. These doped semi-conductors today are widely used in many electrical devices. Some of them are rectifiers, transistors, thermistors, oxides cathodes and photo-sensitive elements. This paper reviews the fundamental concept of impurity in semi-conductors and recent work on doping of the latter. Purification methods are described in the case of group IV elements and semi-conducting intermetallic compounds. Results of different physical measurements have been discussed in order to understand the role of 'doping'.

## Introduction

Semi Conductors can be easily distinguished by their electrical resistance which lies between insulators ( $10^{10}$  ohm cm and upwards) and metals ( $10^{-4}$  ohm cm and below). The extreme sensitivity particularly to the chemical composition is their chief characteristic property. The significance of the chemical composition in semi-conductor—physics goes far beyond the usual usage of this term in chemistry. The chemical difference between two bodies means, to the unbiased reader, the difference, for instance, between cupric oxide ( $\text{CuO}$ ) and cuprous oxide ( $\text{Cu}_2\text{O}$ ). The semi-conductor physicist, on the other hand compares two samples by the magnitude of their electrical properties, where variation of a fraction of a percent in the oxygen content can be of decisive significance—(Dixit and Agashe)<sup>1</sup>. Minute deviations from stoichiometric composition (of the order of  $10^{-4}$ ) may manifest themselves in the electrical resistivity by changes of several orders of magnitude. Similarly, a minute amount of a foreign substance such as chlorine content of the order  $10^{-4}$  in selenium can influence the electrical resistivity decisively. (A.E.G. Mitt. 1956). The addition of boron (0.001%) to highly purified silicon resulted in the production of highly sensitive crystals, which were also resistant to damage by electrical overload (Theuerer)<sup>2</sup>.

The introduction of a foreign substance in a matrix, which makes an insulator a semi-conductor, or which increases the efficiency of a matrix already a semi-conductor, is called 'Doping'. Similar to electrical conductivity changes, the other properties of semi-conductors are also modified by doping. The most significant and important feature of doping is the possibility of changing the conductivity etc. without a simultaneous change in bulk chemical properties.

At absolute zero, a semi-conductor with a perfect crystal lattice has all electrons in the valence band and no electrons in the conduction band, and hence an insulator. In some semi-conductors the forbidden zone between the valence

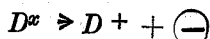
band and conduction band is so narrow that even by the thermal excitation at room temperature, electrons can jump over to the conduction band (intrinsic conduction). While on the other hand, in some of the semiconductors, the forbidden zone is so broad (greater than 1 eV) that electrons cannot cross it by thermal energy. However localised donor terms can be inserted within the forbidden zone near the conductivity level either by impurities or by reversible or irreversible electronic disorder (n type of conductor). Equally acceptor terms can be produced in the same way near the lower edge of the forbidden zone. (p-type of conductor). For example, NiO is a p type of conductor because in thermal disorder it contains excess oxygen and therefore some Ni<sup>3+</sup> ion as acceptor terms. The number of these can be increased by insertion of ions of lower valence (Li<sup>+</sup>, Ag<sup>+</sup>) or decreased by introduction of ions of higher valence (Ga<sup>3+</sup>, Cr<sup>3+</sup>). Correspondingly, ZnO is n type of conductor because of its thermal oxygen deficiency and hence the presence of Zn<sup>0</sup> or Zn<sup>+</sup> as donor levels. These can be increased in number by the insertion of ions of higher valence than Zn<sup>++</sup> (Ga<sup>3+</sup>, Al<sup>3+</sup>) or decreased by lower valence ions (Li<sup>+</sup>).

A particular semi-conductor will not be, however, characterised by one particular type of conduction (p type or n type). Ohl<sup>3</sup> observed that silicon is capable of dual characteristics. Generally the dominant process is considered. It has been found that minority current carriers and energy levels also have a profound significance in certain problems. Further the predominant type of conduction may not prevail throughout the entire temperature range. Impurity semi-conductors would also exhibit intrinsic properties at higher temperatures.

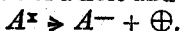
The most of the semi-conductors used today are from (a) IV group elements, (b) intermetallic compounds, III-V group and (c) oxides, sulphides selenides, tellurides. The impurity energy levels occur in a variety of ways. In (a) they occur either due to the introduction of III or V group elements, or by heating them in oxygen. In (b) they occur either by introduction of II, IV, VI group impurities or by stoichiometric excess/deficiency of one constituent over another. In (c), by a departure from the stoichiometric composition.

IV group elements have a diamond type of structure. III-V group compounds have a structure similar to Zinc blend lattice. (Welker<sup>4</sup>). Cadmium selenide (in the case of rectifiers) show Zinc blende type of structure. (Hoffman & Rose<sup>5</sup>). Cu<sub>2</sub>O rectifying layers have a structure nearer to zinc blende type (Dixit and Agashe<sup>6</sup>). When sulphur atoms are replaced by Zn in the zinc blende, the structure becomes diamond type. In a diamond structure, each atom is surrounded by four neighbours. The binding of these four neighbours consists of four electron pair bonds. The bonds consist of the four valence electrons of the atom under consideration together with one of the valence electrons from each of the four neighbouring atoms to which the bond leads. As all the valence electrons are fixed in pair bonds, they will not be available for the conduction process. Now consider the situation when an impurity (III or V group) in germanium is introduced. An arsenic atom (V group) with five outer electrons can replace a germanium atom in the lattice. More specifically, an As<sup>5+</sup> core is substituted in Ge<sup>4+</sup> core. Four of the five outer electrons of the As atom are used up in the four pair bonds for the binding

to the four germanium neighbours which compensates four positive charges of the  $As^{5+}$  core, so that there is one positive charge left to bind the fifth outer electron. This fifth outer electron can be easily removed from the impurity and thus migrates away as a conduction electron. The impurity acts as a source or "donor" of conduction electrons. The entire process can be interpreted as the dissociation of a neutral donor  $D^0$  into a positively charged donor core  $D^+$  and a conduction electron.



Now similarly consider an impurity from III group say In. When a germanium atom is replaced by one Indium atom only three valence electrons are introduced so that one valence electron is missing in the four pair bonds to the four germanium atom neighbours. This vacancy can easily be filled by a valence electron from one of the neighbouring bonds. The process of completing an incomplete pair bond from a neighbouring complete pair bond by the motion of a valence electron allows the vacancy (or what we call the 'hole') to move in the lattice. The indium atom remains in its original place and has now acquired an electron in addition to its original three valence electrons, so that it is negatively charged. This is an example of an impurity, which accepts an additional electron, and is, therefore, called an 'acceptor'. This process includes the liberation of a hole and the charging of the impurity by one negative charge,

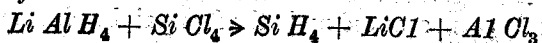


Thus by introducing an impurity we can make an insulator a semi-conductor, either a p type or n type. In the case of deficit semi-conductors ( $Cu_2O$ ,  $ZnO$ ) the impurity (excess or deficiency of one constituent) is introduced automatically in the preparation. Procedure based on thumb rules has to be followed in their preparation. Because the properties of semi-conductors are affected by minute quantities of impurities the first step in their preparation is the purification. This point was emphasised by F. Seitz as early as 1942. We will consider below how the important semi-conductors are made pure and then a controlled impurity is added to it.

### Germanium and Silicon

Germanium is produced in pure form by zone refining method. Six zone passes of an ingot of the then purest commercially available germanium suffice to reduce the impurities to concentrations less than 1 in  $10^{10}$  atoms of germanium (Pfaun and Oslen)<sup>7</sup>. The success of this process with germanium can be attributed to favourable distribution coefficients, the low reactivity of molten germanium and the availability of a suitable crucible material, high purity graphite. A shot (Lesk)<sup>8</sup> is used as a master alloy for controlled impurity addition during growth of germanium crystals. This method gives convenient small pellets with the same impurity fraction in each pellet (in a given batch). Recently Leverton<sup>9</sup> has described in detail a floating crucible technique for growing uniformly doped crystals which can be used for growing large doped crystals of Germanium but not for silicon.

In the case of silicon, the high reactivity and unfavourable distribution coefficients of certain impurities limit the efficacy of the physical zone refining method. The following method has been therefore employed—Silane gas is generated by the reaction:



An advantage of this particular process is that non-volatile impurities are immediately separated. The few which are present in gaseous form are dealt with specifically either by treatment of the reactants or of the resultant silane. For instance, boron, which forms volatile diborane can be retained in the reaction vessel as non-volatile lithium borohydride, if lithium aluminium hydride is maintained in excess. The pure silane is cracked on a hot silicon surface and eventually massive silicon boules are built up. From these boules, single crystals are pulled direct, without any intermediate melting process. This process avoids the possibility of crucible contamination. A molten layer of constant volume is maintained at the top of the boule by a radio frequency heater which couples directly into the silicon. As the crystal is drawn from the melt in the normal CZOCHRALSKI method. The boule is fed upwards to replenish the molten pool. Doped crystals are conveniently produced by mixing appropriate quantities of diborane or phosphine with the silane gas before composition.

Lehovec and Belmont<sup>10</sup> have developed a technique for preparation of p-n junctions by surface melting. This consists essentially in melting a thin skin on the surface of a crystalline wafer of a semi-conductor (germanium), doping the melt to opposite polarity by the introduction of a suitable donor or acceptor element, as the case may be, and subsequently freezing the melting zone from the underlying zone in form of a coherent crystal with a p-n junction formed at the interface of the melt and solid base. Billig and Gasson<sup>11</sup> have modified the method in which fairly fast thermal response enables to control the depth of the molten surface layer (by induction heating) with relative ease. A rod of silicon is slowly moved upwards at a speed of about 4 mm./min through a sharp thermal zone. This causes the molten zone to travel down the length of the rod. On removal from the surface, the skin of the ingot which has been melted and doped is found converted to opposite polarity. The rod is then cut into disks 1 to 2 mm. thick each of which contains a ring type p-n junction. Their results are summarised below:—

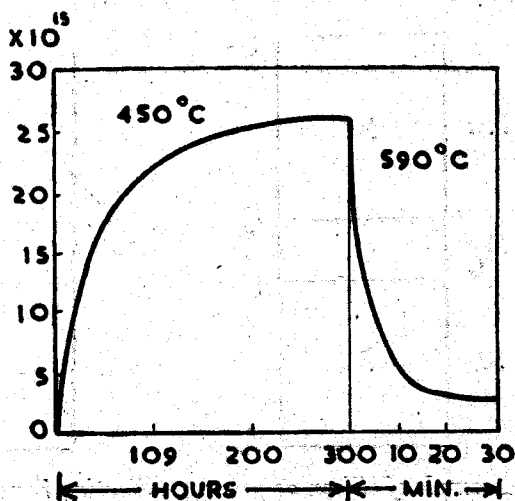


Figure 1—Change of electron concentration with time in the case of Silicon annealed at 450°C and 590°C after Fuller and Logan (Reference 12).

TABLE 1

Type of Silicon	Doping Agent	PI V for 5 mA.
p	Sb in Argon atmosphere	105—115 V.
p	NH <sub>3</sub> at atmospheric pressure	80—140
p	P <sub>2</sub> O <sub>5</sub> in vacuum	135—160
p	Ag in vacuum	110—150
n	Al in vacuum	400—700

The technique of gas doping of silicon has certain advantages in a production process. Fuller et al.<sup>12</sup> prepared silicon crystals under an inert atmosphere by pulling with a rotation from the melts in silica crucibles on heating them in the range 300°C—500°C. Large donor concentrations are formed. These donors are observed by resistivity measurements made at room temperature after annealing. After formation, the donor centre can be removed by heating at a higher temperature (Fig. 1). The change observed in carrier concentration could be interpreted as an increase in donor concentration or loss in acceptor concentration. The identification of the impurity as an acceptor is ruled out, however, since this would require that all retated crystals be compensated with  $2 \times 10^{16}$  acceptors/cm<sup>3</sup> whereas a net impurity unbalance as low as  $10^{14}$ /cm<sup>3</sup> can be readily obtained in pulled crystals.

Kaiser and Keck<sup>13,14</sup> have further studied the doping of silicon by oxygen. A silicon crystal is grown between A and B in a helium atmosphere by means of floating zone equipment. At point B, a small concentration of oxygen was added to helium stream and growth proceeded to C. Purified helium was again used to continue the growth to D. (Fig. 2). The crystal as grown was p type along its full length. After heat treatment at 450°C for five hours the sample area between B and C converted into n type forming two junctions at B and C. These junctions have the interesting feature that they can be erased and regenerated by a proper heat-treatment cycle.

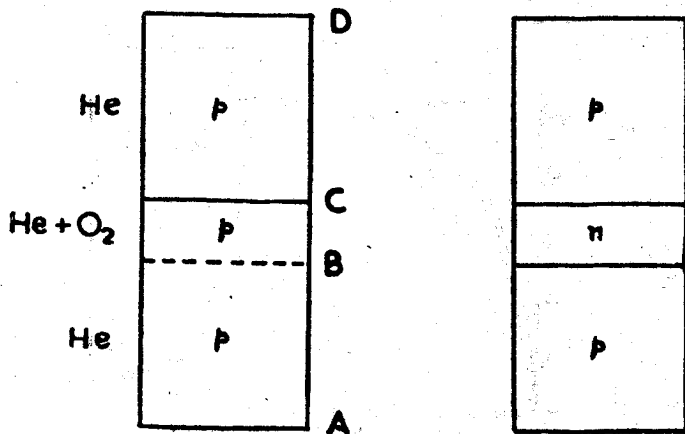


Figure 2.—(a) A sample of silicon as grown in Floating Zone equipment.

(b) The same after heat treatment at 450°C. After Kaiser and Keck (Reference 14).

**Semi-conducting intermetallic compounds (S.I.C.).**

These compounds have attracted attention in recent years mainly because of the possibility that they may prove more efficient in particular applications than germanium or silicon and perhaps lead to quite new devices particularly those with higher carrier mobility (Pincherle and Radcliffe<sup>15</sup>).

In the purification of the constituents of these compounds one or more of the refining processes (filtration, distillation and zone refining) may be combined with a chemical method. Sometimes when the chemical refining involves the production of an intermediate compound, it is convenient to use a physical refining method on the intermediate compound before it is decomposed.

The fusion of the elements and the zone refining of the semiconductor compound can be quite straight forward when vapour pressures are low and when the maximum melting point occurs at stoichiometric composition. When large vapour pressures are encountered, special techniques are necessary, for example, zone refining may be carried out under a controlled pressure of one constituent. Where stoichiometric difficulties arise, crystal growth by deposition from the vapour phase may be the only answer, though this method of growing crystals is more difficult to control than melt techniques. There is the possibility that the crystals produced will have lower defect concentrations, for growing the crystals by deposition is virtually free of constraints and the temperature at which growth takes place is considerably below the melting point. Lead selenide crystals have been prepared by this method by controlling the vapour pressure of selenium. Both p and n type crystals of desired carrier concentration may be produced.

Doping to achieve the desired effects is accomplished in the same manner as in the case of germanium and silicon, though it is a long way to go before attaining the perfection that has been only reached in Ge and Si. There are well established results only for III—V compounds. In this case, elements of group II (Mg, Zn) are found to act as acceptors, while group VI elements (Se, Te) act as donors. The unusual possibility also exists in this case that a group IV element may act as either a donor or an acceptor depending upon whether it substitutes in the lattice for a group III or a group V atom. A detailed study in this case would also be useful to the understanding of the structure of these substances.

This detailed study has been done only in the case of In Sb. An atom of say Pb. should act as an acceptor on a site normally occupied by atom of group V and as donor in the other site. Welker<sup>16</sup> argues that a large atom such as Pb would substitute the larger ion and thus would be preferably in the In sites in InSb, making it n type, but in the Sb site in AlSb making it a p type. Substitution of one of the components with another element from the same column does not appear to have any marked effect on the electrical properties. It would appear that other factors such as relative electro-negative properties might also play a significant role.

Little is known of the properties of interstitial foreign atoms as well as those of vacant lattice sites and interstitial atoms of the compound elements. It is known, however, that some compounds when first produced or zone refined are always of the same type, p or n. It seems probable that this is due

to a loss of the element with the higher vapour pressure at the temperature at which the compound is formed. The vacant lattice sites thereby formed would behave as donors or acceptors or traps, and the study of the radiation effects may prove useful in elucidating this point. This has been studied in the case of InSb by Cleland and Crawford<sup>17</sup> under neutron irradiation. Both transmutation and disorder effects were observed. Sn was produced by the transmutation and behaved as a donor, confirming Welker's speculations, since p crystals became n. The defects produced by fast neutrons acted as electron traps in 'n' type of material but it is not known whether they act as acceptors in 'p' type crystals.

We have considered the first two types namely IV group element and semiconducting intermetallic (S.C.I) Compounds. Now we will consider the other type of semiconductors *viz.* oxides, sulphides and the effects of impurities in it. The impurities in this case are also stoichiometric departures or foreign atoms. Cuprous oxides and cupric sulphides are known as rectifiers. These compounds as electrical devices have gone to the background due to the extraordinary success of Silicon, germanium and due to the promise of success in S.C.I. Compounds. However many of these substances (ZnO etc.) are used as catalysers in chemical reactions and we will examine some of the recent work in catalysis on doped semi-conductors, and see how the phenomenon of catalysis helps us in increasing our knowledge of doping a semi-conductor.

### Catalytic Action

The possibility of changing the conductivity and the concentration of current carriers by 'doping' without a simultaneous change in the bulk chemical character enables one to study the catalytic behaviour as a function of this parameter. The idea of correlating semi-conducting properties and catalytic action presupposes that catalysis has something to do with the electronic state of the solid. In large number of reactions the catalytic activation consists in a transfer of electrons from the molecule to the catalyst or vice versa. The reactions can be divided into two groups, Donor reactions in which electrons are transferred to the catalyst. Hydrogenation and dehydrogenation clearly belong to this group. Metals having many free electron levels are good catalysts for these reactions. The second group contains acceptor reactions involving molecules with high electron affinity such as  $O_2$  or  $H_2 O_2$ .  $H_2 O_2$  decomposition is catalysed also in homogeneous systems by electron addition.

The task of connecting semi-conductor properties to catalytic action reduces to the question whether donor reactions are catalysed by p-type conductors and acceptor reactions by n-type conductors. According to the above principle, an increase of p type conduction enhances the donor reaction catalysis and vice versa. Enhancing a reaction means increasing its rate or lowering its activation energy (Schwab<sup>18</sup>).

Wagner<sup>19</sup> showed that the decomposition of nitrous oxide ( $N_2O$ ) improves if  $Ga_2 O_3$  is added to zinc oxide which is used as a catalyser. Schwab and Block<sup>20</sup> have carried out systematic investigation with doped catalysts. They studied the carbon monoxide oxidation with Li and Cr doped

NiO and with Ga and Li doped ZnO. With NiO they found that the activation energy drops on addition of  $\text{Li}^+$  and increases on addition of  $\text{Cr}^{3+}$  i.e. it is the lowest at the highest positive hole concentration. However with ZnO as a catalyst  $\text{Li}^+$  increases and  $\text{Ga}^{3+}$  decreases the activation energy. Block and Chou<sup>21</sup> have confirmed these results by using CoO (p conductor) as catalyst. However at high oxygen pressures this catalyst is self-poisoned, ( $\text{Co}_3\text{O}_4$  is formed which is n type conductor).

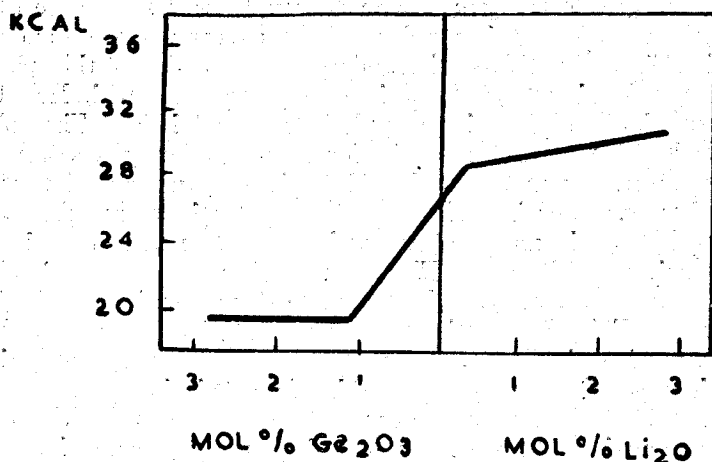


Figure 3—Activation energy for catalytic oxidation of CO on doping ZnO with Ga and Li. After Schwab and Block (Reference 20).

Another interesting example is ethylene hydrogenation with pretreated chromic oxide (Voltze and Weller<sup>22</sup>). Pretreatment with the acceptor  $\text{O}_2$  increases the conductivity which is characteristic for a p type conductor. However  $\text{O}_2$  poisons the hydrogenation. This would be contradiction if it were not reasonable to assume that  $\text{O}_2$  chemisorption produces a double layer on the surface, the negative outside of which repels the hydrogen electron. On the other hand hydrogen chemisorption decreases the conductivity by filling up of the positive holes and increases the rate of hydrogenation because this chemisorption process is just identical with hydrogen activation.

In the above examples electrons and positive holes exerted a catalytic action because they could come to the surface by thermal excitation. From this, one immediately would like to know whether a photosensitive semiconductor will become a catalyst on illumination at temperatures at which it is not catalyst. Pure zinc oxide, entirely inactive in dark, decomposes  $\text{H}_2\text{O}_2$  when illuminated with white light (Hnojewy<sup>23</sup>).

### Concluding Remarks

We have so far seen how doping is helpful in the case of semi-conductors. The most important advantage of doping is that the same material with different impurities can be used in a variety of ways. Particularly in the case of transistors a material having different carrier concentrations in different regions is an advantage. This condition could be adequately fulfilled by suitable doping. It has been shown in the case of oxide cathodes by Peterson



et al<sup>24</sup> and Ritter<sup>25</sup> that the activation of cathodes results solely from reaction of base impurities with the coatings and their diffusion in the oxide layer. The emission could, therefore, be controlled by surface concentration of metals. The catalytic action solely depends upon surface. It has been shown by Serian<sup>26</sup> that heat-treatment of impurity semi-conductors may generate a depletion of impurities near the surface and thus influence the properties.

The electrical conductivity measurements coupled with knowledge of Hall Coefficients give us an idea of the number and sign of current carriers and also of the mobilities. The infrared absorption and reflection studies of thin plates of semi-conductors give the magnitude of the energy gap, and with Hall Coefficients they are able to give us the mass of electrons and holes. The effective mass also can be determined from ionisation energy of impurity atoms (Seraphin)<sup>27</sup>. Magnetic measurements are also able to give very important information. A theoretical treatment of the various contributions by the atoms, free carriers and the impurities to the magnetic susceptibility of a semi conductor has been given by Busch and Mooser<sup>28</sup>. The diamagnetism due to free carriers is temperature dependent, and can be separated from atomic contribution in pure specimens. This gives us the values for the activation energy. In the case of gray tin, the behaviour of susceptibility in impure specimens is characteristic of the type of centres. One can thus know which centres arise from the introduction of given foreign atoms. Magnetic susceptibilities of iron doped germanium have been determined, these measurements have given some idea of the effect of impurities on the susceptibilities of semi-conductors. The susceptibility of semi conducting and insulating  $\text{Cu}_2\text{O}$  have also given us an idea of the excess of oxygen (deficit of copper) required for semi-conduction. In the case of titanium dioxide rectifiers surface reduction is done by hydrogen at 560°C. Susceptibility increase has been observed simultaneously. It has been interpreted as being due to the change consequent upon the removal of  $\text{O}_2^-$  ions from the lattice as water molecules (Gray)<sup>29</sup>.

Cyclotron resonance experiments on InSb at room temperatures yield an effective electron mass  $m^* = 0.015 m$  as compared with the value of 0.025  $m$  determined by transport phenomena. The discrepancy has not yet been explained. Paramagnetic resonance experiments on silicon carbide crystals show that the three resonance peaks are obtained when the crystals are doped with nitrogen and only one peak when doped with aluminium or boron. An explanation based on equilibrium probabilities for electron trapping by singly or multiply charged defects is that the trapped electron can be in an 's' state and near a nitrogen nucleus.

The most rational model for the semi-conductor catalyst comprises an aggregate of crystallites possessing surfaces and grain mosaic boundaries differing significantly from the interior constitution. The phenomena of doped catalysts can also be very well understood from magnetic measurements. The introduction of foreign ions into a substance changes the ionisation state of some of the lattice ions. This will be reflected in magnetic properties. It is reasonable to assume that the valence control impurities could be studied as a function both of semi-conductivity and magnetic susceptibility changes. (Selwood)<sup>30</sup>.

All the above measurements give us to a large extent the nature of semi-conductors, and this helps to decide in what way a particular semi-conductor can be used in electrical devices. However this gives a scanty information about the process that has changed the properties.

A large group of compounds in which  $Sp^3$  tetrahedral bonds occur and whose structures are closely related to zinc blende lattice are semi-conductors (Mooser and Pearson)<sup>31</sup>. The question of bond relationships in such type of conductors has been discussed mainly on the concept of electronegativity (Goodman & Douglas)<sup>32</sup>. Though this explains how impurities make an insulator a semi-conductor, the questions still remain-how many atoms of impurities have actually substituted the parent atoms? and how is their distribution? Does any ordering take place with respect to the impurity introduced? In many cases it is quite known that some heat-treatment or annealing or surface etching is necessary. Does this induce an order? We have seen that in the case of silicon, heating the crystal within a particular range of temperature gives us a particular type of semi-conductor. According to Kaiser<sup>13</sup> the heat treatment produces  $SiO_4$  complexes. It is quite likely that in the process of manufacture and doping of a semi-conductor, a fixed number of foreign atoms gets associated with one grain of parent material. In copper oxide rectifiers, it has been shown that one oxygen atom (or copper defect) is associated with one grain of  $Cu_2O$  comprising of 120 molecules (Dixit & Agashe)<sup>33</sup>. The question of order and grain size in doped semi-conductors when studied with the help of X-ray & Neutron diffraction techniques, may therefore be able to throw more light as regards the impurity to be introduced and further treatment to be given to a semi conductor. The neutron diffraction technique (within its limitation) would be particularly useful where X-ray scattering coefficients for the parent atoms and impurity atoms are nearly the same (Agashe)<sup>34</sup>. This knowledge would enable us to interpret the thumb rule methods practiced many times in the manufacture of doped semi-conductors.

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