

4. They have negative temperature coefficient of resistance ( $\alpha$ ) i.e. with the increase of temperature their resistivity decreases or conducting increases rapidly.
5. The electrical conductivity of semiconductor is very much affected by even very minute amount of impurity added to it. This process of adding impurities is called as “Doping”.

Examples of Semiconductors are Silicon, Germanium, PbS, BaO, Fe<sub>3</sub>O<sub>4</sub>, InSb, etc.

**Types of semiconductors:**

These are mainly of two types (Puri and Babbar, 2005):

1. Intrinsic semiconductor
2. Extrinsic semiconductor

**Intrinsic semiconductor:**

Pure semiconductors are called intrinsic semiconductor and are also called as undoped semiconductor or I-type semiconductor. In intrinsic semiconductor the number of electrons reached the conduction band with the same number of holes leaves in valence band that means the number of electrons is equal to number of holes.

$$N_e = N_p = N_i$$

where,  $N_e$  is Electron carrier concentration,  $N_p$  is Hole carrier concentration and  $N_i$  is intrinsic carrier concentration.

Mathematically, the holes concentration in valence band is given as

$$P = N_v \exp \left[ -\left( \frac{E_F - E_V}{k_B T} \right) \right] \quad (1)$$

And, electron concentration in conduction band is given as

$$N = N_c \exp \left[ -\left( \frac{E_C - E_F}{k_B T} \right) \right] \quad (2)$$

where,  $k_B$  is Boltzmann constant,  $T$  is absolute temperature of intrinsic semiconductor,  $N_c$  is effective density of states in C.B. and  $N_v$  is effective density of states in V.B.

So, the total current in intrinsic semiconductor is equal to the sum of hole and electron current i.e.

$$\text{Total current} = \text{Electron current} + \text{hole current}$$

$$I = I_{\text{hole}} + I_{\text{electron}}$$

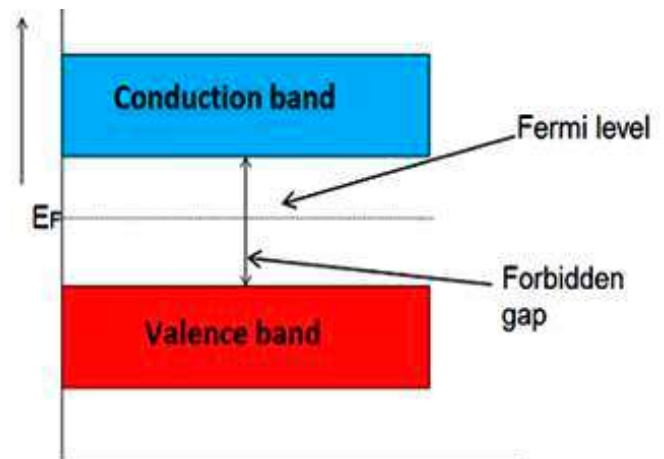
**Fermi level:**

Fermi level is basically the probability of occupation of energy levels in valence band and conduction band. At 0 K, intrinsic semiconductor behaves as perfect insulator. However, with the increase in temperature, holes and free electron are generated.

As  $N_e = N_p$ , the probability of occupation of energy levels in C.B. and V.B. are equal due to which the Fermi level for pure semiconductor lies in the middle of forbidden band.

Fermi level lies in the middle of forbidden band it shows that the concentration of free electron is equal to that of holes.

The number of holes in V.B. is dependent on the effective density of states in V.B. and the distance from the Fermi level in the given valence band.



The expression for Fermi level (Arora and Hemne, 2015) in intrinsic semiconductor is given as

$$E_F = \frac{E_c + E_v}{2}$$

where,  $E_F$  is Fermi level,  $E_c$  is Conduction band and  $E_v$  is Valence band.

### Extrinsic semiconductor:

The semiconductor in which impurities are added is called extrinsic semiconductor. Extrinsic semiconductor has high electrical conductivity than intrinsic semiconductor (Arora and Hemne, 2015). The number of free electrons and holes in extrinsic semiconductor are not equal.

**1. Silicon (Si):** Silicon was discovered by a Swedish chemist Jons Jacob Berzelius in 1824. Silicon is a chemical element with symbol (Si) and atomic number 14. It has two electrons in K-Shell, 8 electrons in L-shell and 4 electrons in M-shell. Electronic configuration-  $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$  (Gupta and Kumar, 2018). It is a member of group 4 and a p-block element. Its melting point and boiling point are 1687 K and 3538 K, respectively. It is hard-brittle crystalline solid with a blue-grey metallic lustre. Silicon is the second most abundant element in the earth's crust and seventh most abundant element in the universe. Silicon is found in nature with oxygen in the form of silicon dioxide. It commonly takes the form of sand but also exists as quartz, rock crystal and agate.

It is used as pure semiconductor in solid state devices in microelectronics. It can be doped with Boron, Gallium, Phosphorous or Arsenic to produce silicon for use in transistor-solar cell, rectifier and other solid state devices.

**2. Germanium:** Germanium was one of the elements whose existence was predicted by Russian chemist Dmitri Mendeleev in 1869. In 1886, Germanium was discovered by Clemens A. Winkler. Germanium is a chemical element with the symbol (Ge) and atomic number 32. Its electronic configuration is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^2$ . Its boiling point and melting points are 3106 K and 1211.40 K respectively. It is a lustrous, hard-brittle and it is a greyish white metalloid. Germanium belongs to p-block, group 14 and period 4.

Abundance of Germanium in earth's crust is about 1.6 parts per million by weight and abundance in the solar system is about 210 parts per billion by weight. Germanium is found in germanite, argyrodite and zinc ores. It is also found in silver lead and copper ores.

It is used as pure semiconductor in transistor and other electronic devices. The major uses of germanium are Fibre-optic system infrared optics, solar cell and LED. Germanium are also used for polymerization catalysts and making of nanowires.

**Extrinsic semiconductors are classified in to two types:**

**N-type semiconductor:** In n-type semiconductor, added pentavalent impurity in an intrinsic or pure semiconductor. Phosphorus, arsenic, antimony etc. are pentavalent impurities and are donor impurity (Gupta and Kumar, 2018).

**P-type semiconductor:** In intrinsic or pure semiconductor, added trivalent impurity then it is said to be p-type semiconductor. Boron, Gallium, Indium, and Aluminium are the examples of trivalent impurity and are called acceptor impurity (Gupta and Kumar, 2018).

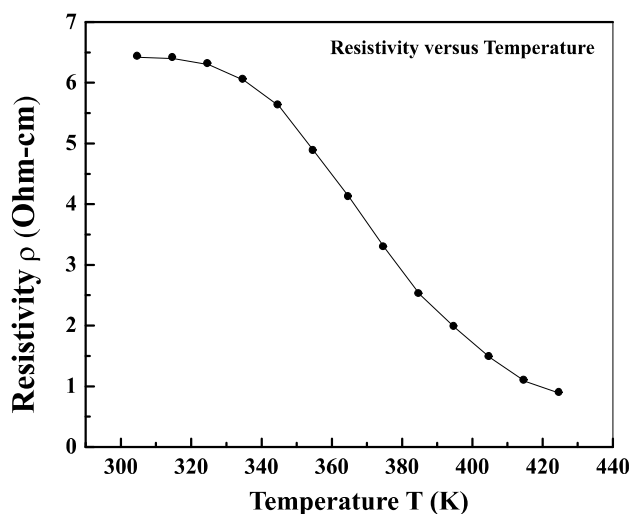
In this report, intrinsic semiconductor crystals Si and Ge are chosen to study their electrical properties, band gap, crystal structure, interatomic separation and density (Arora and Hemne, 2015).

### Materials and Methods:

The resistivity versus temperature measurements were carried out by four probe method. The band was also calculated by the plot of  $\log \rho$  versus  $T^{-1}$  and was measured by four probe method. The crystal structure was examined by X-ray diffraction measurements at room temperature. For X-ray diffraction measurements, RIGAKU miniflex 600 X-Ray diffractometer (XRD) has been used. Semiconductor crystals Si and Ge were cleaned by acetone and de-ionized water before performing electrical measurements and X-ray diffraction measurements.

## Results and Discussion:

**Resistivity versus Temperature Data:** The resistivity versus temperature measurements were performed on Germanium semiconductors. For this measurement we have taken  $I = 0.05A$ . The temperature was varied from 32°C. (close to room temperature) 152°C. to . Table -1 shows the resistivity of Ge semiconductor at different temperatures. The resistivity versus temperature graph is shown in Fig. 1.



**Fig. 1. The resistivity versus temperature data for Ge semiconductor**

The following graph shows the variation of resistivity with temperature. From the graph it is clear that at room temperature (~300 K) the resistivity is maximum with ~6.5 Ω-cm and above 300 K (Gupta and Kumar, 2018), it decreases non-linearly. At 420 K, resistivity drops to ~1 Ω-cm. The electrical resistivity of materials is related to temperature by relation (Puri and Babbar, 2005):

$$\rho(T) = \rho_0 [1 + \alpha(T - T_0)]$$

where  $\alpha$  a temperature coefficient of resistivity,  $T_0$  it is a fixed reference temperature,  $T$  is temperature at which resistivity needs to be found out and  $\rho_0$  resistivity at temperature  $T_0$ . As we know that, with the rise in temperature the number of current carriers increases rapidly which in turn

increases the conductivity and decreases the resistivity. Thus, we can say that the temperature coefficient of resistivity for semiconductors is negative.

### Band Gap of Ge Semiconductor:

The band gap generally refers to the energy difference in electron (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become a conduction electron which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current.

### Determination of Band Gap of Semiconductor:

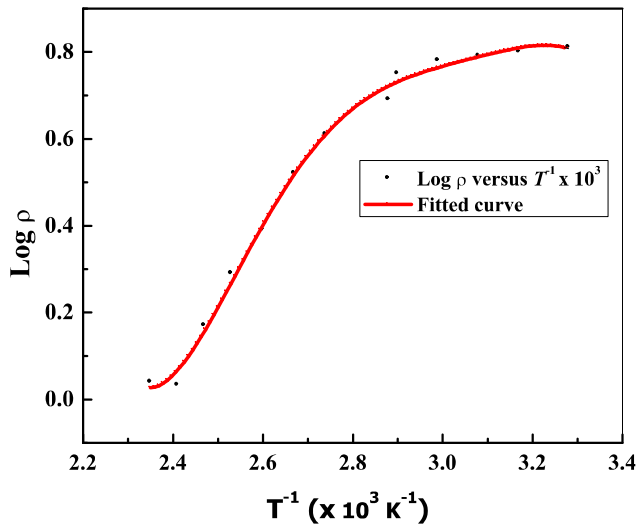
**Four Probe Method:** In this method, four probes are placed on a flat surface of the materials to be measured. Current is passed through the two outer electrodes. The floating potential is measured across the inner pair. The semiconductor may be considered to be a semi- infinite volume if the flat surface in which the probes root is adequately large. The surface on which the probes rest may be mechanically lapped in order to prevent minority carrier injection and to make good contact.

Taking  $T^{-1} \times 10^3$  along x-axis and  $\log \rho$  along y-axis, we have plotted a graph between  $\log \rho$  and  $T^{-1} \times 10^3$  for 13 different values of voltages and temperatures. As we can see, there is a gradual increase in the  $\log r$  values as  $T^{-1} \times 10^3$  increases.

This happens because the band gap of a semiconductor is the minimum energy requires executing an electron that is stuck in its bound state into a free state. From the graph data we can conclude that at different voltages and temperature the value of  $r$  is changing ; high voltage with low temperature increases in temperature, the voltage drops and with drop in voltage the value of ohm-m i.e.  $r$  and  $T^{-1} \times 10^3$  and  $\log r$  value decreases.

**Table 1. Calculation of resistivity of Germanium at different temperature keeping current, I=0.5 mA.**

Sr. No.	T (°C)	V (V)	T (K)	$\rho$ ( $\Omega$ -cm)	$T^{-1} \times 10^3$	$\log \rho$
1.	32	150.8	305	6.42	3.28	0.81
2.	42	149.9	315	6.40	3.17	0.80
3.	52	147.7	325	6.30	3.08	0.79
4.	62	141.8	335	6.04	2.99	0.78
5.	72	131.8	345	5.62	2.90	0.75
6.	82	144.4	355	4.87	2.88	0.69
7.	92	96.5	365	4.11	2.74	0.61
8.	102	76.9	375	3.28	2.67	0.52
9.	112	58.9	385	2.51	2.60	0.39
10.	122	46.3	395	1.97	2.53	0.29
11.	132	34.4	405	1.47	2.47	0.17
12.	142	25.4	415	1.08	2.41	0.033
13.	152	20.7	425	0.88	2.35	0.04



**Fig. 2. The versus  $T^{-1} \times 10^3$  plot for Ge semiconductor**

**Calculation of band gap of semiconductor:**

$$\text{Slope} = \frac{dy}{dx} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$= \frac{0.692 - 0}{2.8 - 2.4} = 1.73$$

Since slope of the graph between and  $\frac{1}{T}$  is  $\left(\frac{E_g}{2k_B}\right)$ .

Therefore, energy gap

$$(E_g) = 2k_b \times 2.303 \times 10^{+3} \times \text{slope}$$

$$= 2 \times 8.6 \times 10^{-5} \times 2.303 \times 10^3 \times 1.73 = 0.69\text{eV}$$

**X-Ray Diffraction data**

XRD is a rapid analytical technique. It is primarily used for the identification of crystalline material and which give information about unit cell dimension. It is now a common technique for the study of crystal structure and atomic spacing. It is a technique based on constructive interference of monochromatic X-rays. The X-rays are generated by a cathode ray tube which are the filtered to produced monochromatic radiation, collimated to concentrate and then directed towards sample. The interaction of incident X-rays of the sample produces constructive interference which satisfied the condition of Bragg's law (Puri and Babbar, 2005):

$$n\lambda = 2d\sin\theta$$

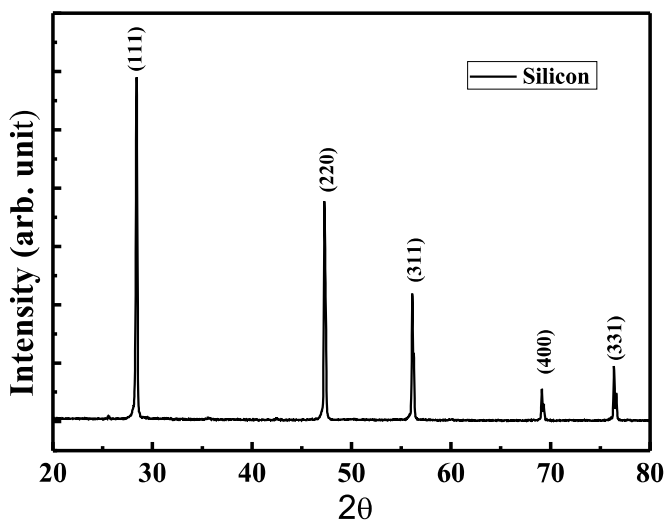
where,  $\lambda$  is the wavelength of the x-ray, d is the spacing of the crystal layers, path difference,  $\theta$  is the incident angle (angle between incident ray and scatter plane), and n is an integer.

This principle of Bragg's law is applied in the construction of instruments such as Bragg's spectrometer, which is often used to study the structure of crystals and molecules.

**Crystal Structure of Silicon Semiconductor:**

The X - ray diffraction data of Silicon semiconductor is shown in Fig. 3. In the following graph, we observe that distinct peaks are formed corresponding to different set of (hkl) values, angle

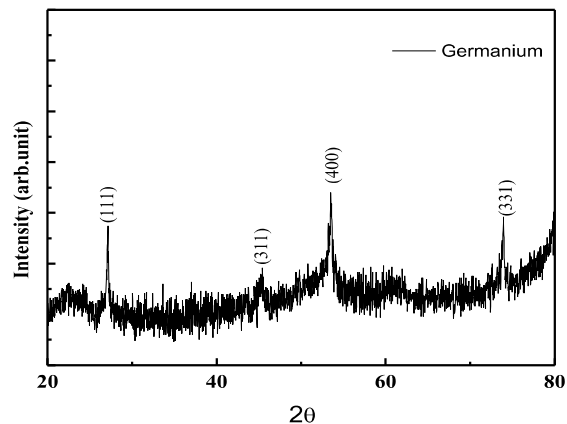
is varied from 20° to 80°. The values of  $\lambda$  and  $n$  is 1.54 Å and 1 (first order), respectively. There are total five Bragg-peaks obtained corresponding to (111) (220) (311) (400) and (331) set of miller indices (Zaumseil, 2015). These peaks belong to diamond cubic structure. The calculated lattice parameters (by using Bragg's law) of Silicon crystal are  $a = b = c = 5.44\text{Å}$ ,  $\alpha = \beta = \gamma = 90^\circ$ .



**Fig. 3. The X-ray diffraction data of Silicon semiconductor**

**Crystal Structure of Germanium Semiconductor:**

The X-ray diffraction data of Germanium semiconductor is shown in Fig. 4. In the following graph, we observe that distinct peaks are formed corresponding to different set of (h k l) values, diffraction angle is varied from 20° to 80°. The Cu-Ka source of wavelength 1.54Å is used. The first order Bragg-peaks corresponding to Miller indices (111), (311), (400) and (331) are shown in the XRD pattern (Pillai, 2018). These peaks belong to diamond cubic structure. The calculated lattice parameters (by using Bragg's law) of Germanium crystal are  $a = b = c = 5.6\text{Å}$ ,  $\alpha = \beta = \gamma = 90^\circ$ .



**Fig. 4. The X-ray diffraction data of Germanium semiconductor**

**Crystallite Size of Silicon and Germanium:**

Crystallite size is the smallest –most likely single crystal in powder form. The crystallite size is commonly determined by X-ray diffraction data. Grain is either a single crystalline or polycrystalline material, and is present in bulk or thin film.

The crystallite size of the thin film samples can be easily calculated from Scherrer formula. The Scherrer formula is given by

$$\tau = \frac{0.9\lambda}{\beta \cos\theta}$$

where,  $\tau$  is Average crystallite size,  $\beta$  is line broadening in radians,  $\theta$  is Bragg angle and  $\lambda$  is X-ray wavelength.

$$\tau = \kappa\lambda/\beta\cos\theta$$

**For Silicon:** For the Bragg peak at  $2\theta = 28.45^\circ$

Wavelength of X-ray,  $\lambda = 1.54\text{Å}$

Line broadening at half of maximum intensity,

$$\begin{aligned} \beta &= 28.50^\circ - 28.32^\circ = 0.18^\circ \\ &= 0.18 \times \frac{3.14}{180} = 0.00314 \text{radian} \end{aligned}$$

Therefore, the crystallite size,

$$\tau = \frac{0.9 \times 1.54\text{Å}}{0.00314 \times \cos(14.225)} = 455.37\text{Å}$$



Thus, the crystallite size of the Silicon crystal is around 455 Å.

**For Germanium:** For the Bragg peak at  $2\theta = 27.123^\circ$

Wavelength of X-ray,  $\lambda = 1.54 \text{ \AA}$

Line broadening at half of maximum intensity,

$$\begin{aligned}\beta &= 27.24^\circ - 26.94^\circ = 0.30^\circ \\ &= 0.3 \times \frac{3.14}{180} = 0.00523 \text{ radian}\end{aligned}$$

Therefore, the crystallite size,

$$\tau = \frac{0.9 \times 1.54 \text{ \AA}}{0.00523 \times \cos(13.54)} = 272.58 \text{ \AA}$$

Thus, the crystallite size of the Silicon crystal is about 273 Å.

### Conclusions:

The structural and electrical properties (resistivity and band gap) of intrinsic semiconductor crystals such as Si and Ge were obtained by X-ray diffraction and resistivity measurements. These semiconductors crystallize in diamond cubic structure. The lattice constants of the Silicon semiconductors are  $a = b = c = 5.44 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . The lattice constant of Germanium semiconductors  $a = b = c = 5.6 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . The crystallite sizes of the Silicon and Germanium crystal for the (111) peak are observed to be about 455 Å and 273 Å respectively. The resistivity versus temperature measurement of Germanium crystal was also performed by four probe method. The room temperature resistivity of Germanium semiconductor is  $\sim 6.5 \Omega - \text{cm}$  and above 300, its value decreases. At 420 K, resistivity drops to  $\sim 1 \Omega - \text{cm}$ . The band gap of germanium crystal is also calculated by plotting  $\log r$  versus  $T^{-1}$ . The observed value of band gap is 0.69 eV at room temperature.

### Acknowledgements:

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### References:

- Arora C.L., Hemne P.S. (2015). *Physics For Degree Students*. S. Chand Publications (P) Limited, New Delhi.
- Gupta S.L., Kumar V. (2018). *Solid State Physics*. K. Nath & Co., Meerut.
- Pillai S.O. (2018). *Solid State Physics*. New Age International (P) Limited, New Delhi. 8<sup>th</sup> Edition.
- Puri V.K., Babbar R.K. (2005). *Solid State Physics*. S. Chand Publications (P) Limited, New Delhi.
- Zaumseil P. (2015). High-resolution characterization of the forbidden Si 200 and Si 222 reflections. *J. Appl. Cryst.* 48. 528-532.