# Determining resistivities and energy band gaps of semiconductors

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This experiment primarily deals determination of various properties related to different types of semiconductors. Those properties are further determined by employing diverse instrumentation. The physics of this experiment is deeply connected to the unusual properties of semiconductors (due to valence band theory) and two major exploitable properties of them are dealt with. The four-probe arrangement is used to find resistivities of n-Al, n-Si and n-Ge thin slice-non-conducting surfaces with a Ge wafer being used to determine the energy band gap of Ge using temperature dependence of resistivity as well. The concept of direct and indirect energy band gaps is discussed and then the UV-Vis spectrophotometer is used to to find more energy band gaps for semiconductors like Zno and a polymer. An article usually includes an abstract, a concise summary of the work covered at length in the main body of the article. It is used for secondary publications and for information retrieval purposes.

*It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles...*

**Isaac Newton**

————————————————

## I. INTRODUCTION

The four-probe method is one of the standard and most commonly used method for the accurate measurement of resistivity. It overcomes the problem of contact resistance and also offer several other advantages. Accurate resistivity measurement in samples having a variety of shapes is possible by this method. The pressure contacts provided in the four-point arrangement are especially useful for quick measurement. This setup can measure samples of reasonably wide resistivity range (micro ohm to mega ohm).

The second part of the experiment is employs a UV-Vis spectrophotometer to determine the energy band gaps of semiconductors. UV spectroscopy or UV–visible spectrophotometry (UV–Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. This means it uses light in the visible and adjacent ranges. The instrument used in ultraviolet–visible spectroscopy is called a UV/Vis spectrophotometer.

## II. AIM

The aim of this experiment is to determine resistivities and energy band gaps of semiconductors using the four-probe, and also performing the latter using a UV-Vis spectrophotometer.

## III. APPARATUS

The apparatus used throughout the experiment is:

1. PID Controller with a Oven Unit, Model PID-TZ

2. Constant Current Sources:-

   - Constant Current Source, Model CCS-01
   - Low Current Source, Model LCS-02

3. D.C. Microvoltmeter, Model DMV-001

4. Four Probe Arrangement with Thermocouple sensor and suitable connectors for DMV and CCS/ LCS.

5. Set of test samples and emery powder for the four-probe

6. An UV-Vis spectrophotometer for the second part of the experiment

## IV. EXPERIMENTAL SET-UP

The experimental set-up for the four-probe part of the experiment is given below.

### A. PID-TZ Controlled Oven

The unit is a high quality PID (Proportional, Integral and Differential) controller wherein the temperatures can be set and controlled easily. The P, I and D parameters are factory set ( $P = 1.8$, $I = 300$, $D = 80$) for immediate use, however, the user may adjust these for specific applications as well as auto-tune the oven whenever required.

### B. Constant Current Source, Model : CCS-01

It is an IC regulated current generator to provide a constant current to the outer probes irrespective of the changing resistance of the sample due to change in temperatures. The basic scheme is to use the feedback principle to limit the load current of the supply to preset maximum value. Variations in the
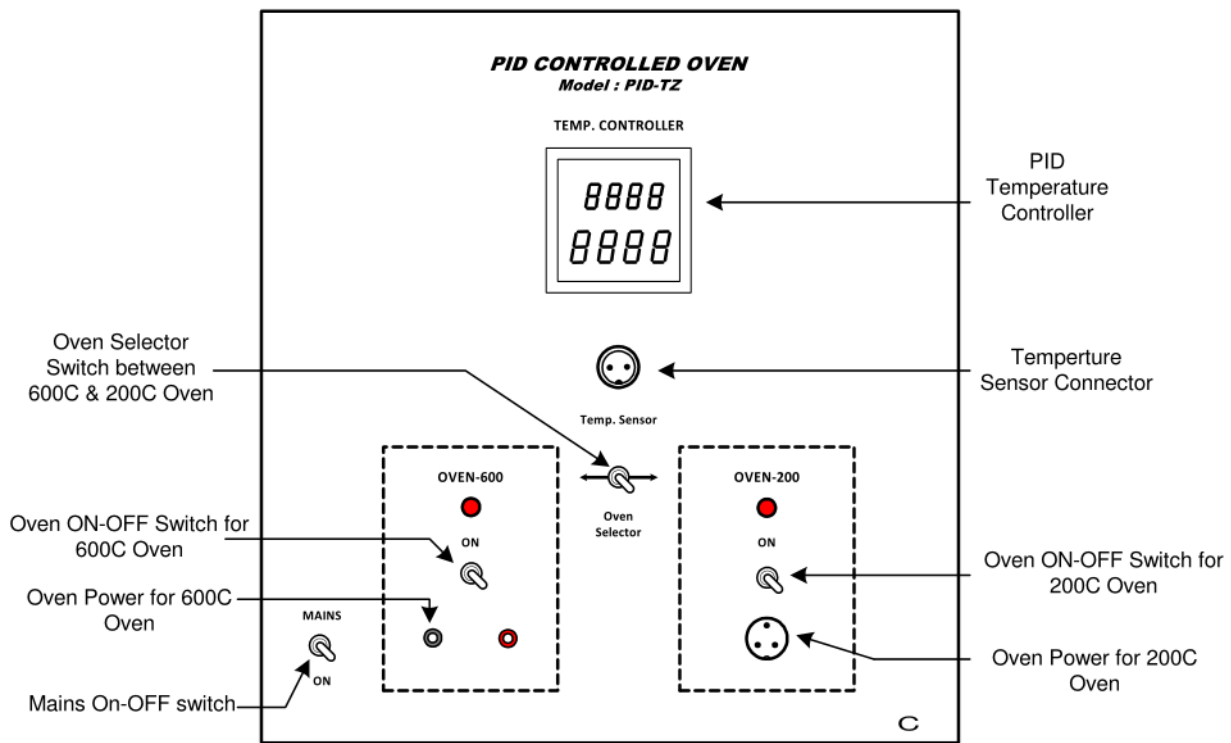
FIG. 1. PID Controlled Oven, PID-TZ

current are achieved by a potentiometer included for that purpose. The supply is a highly regulated and practically ripples free *DC* source. The constant current source is suitable for the resistivity measurement of thin films of metals/ alloys and semiconductors like germanium.

### C. Low Current Source, Model : LCS-02

Low Constant Current Sources are needed when the sample resistance, either inherently or due to contact resistances, is large. These include the resistivity measurement of silicon wafers or high resistivity film deposits.

### D. DC Microvoltmeter, Model DMV-001

Digital Microvoltmeter, DMV-001 is a very versatile multipurpose instrument for the measurement of low *DC* voltage. It has 5 decade ranges from $1\,\mathrm{mV}$ to $10\,\mathrm{V}$ with 100% overranging. This instrument uses a very well designed chopper stabilized IC amplifier. This amplifier offers exceptionally low offset voltage and input bias parameters, combined with excellent speed characteristics.

### E. Four Probes Arrangement

It has four individually spring loaded probes. The probes are collinear and equally spaced. The probes are mounted in

a teflon bush, which ensure a good electrical insulation between the probes. A teflon spacer near the tips is also provided to keep the probes at equal distance. The probe arrangement is mounted in a suitable stand, which also holds the sample plate and RTD sensor. This stand also serves as the lid of PID Controlled Oven. Proper leads are provided for current, Voltage and Temp. measurement with their universal connectors. For current measurement there is three pin connector which can be connected to the CCS-01/ LCS-02 as per requirement of sample. For voltage measurement BNC connector is used connected to DMV-001 unit. For temperature measurement, a two pin connector is provided for connection with PID- Controlled oven unit PID-200 at connector marked as Temperature Sensor. Three levelling screws are provided in Four Probe arrangement by which we can adjust the level of plateform to make it horizontal. A probe holding screw is provided at the collar of the arrangement. Initially it should be in loose position, to allow free movement of Probe Pipe. After placing the sample the Probe Pipe should be lowered so that all four pins touches the sample. The pipe is further pressed very lightly so that the assured firm contact is made of all Four Pins with the sample. The probe holding screw is tightened at this position making the arrangement ready to use.

## V. THEORY

Four sharp probes are placed on a flat surface of the material to be measured (figure (6)). The current is passed through the two outer electrodes, and the floating potential is mea-
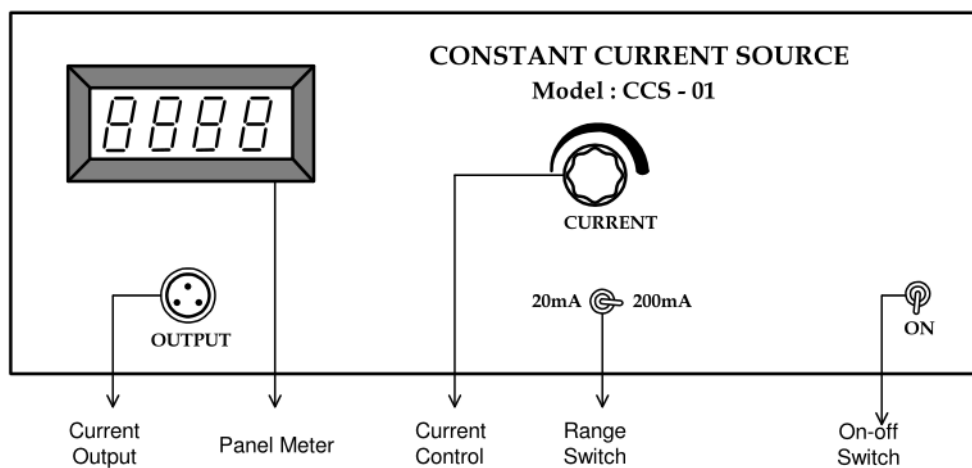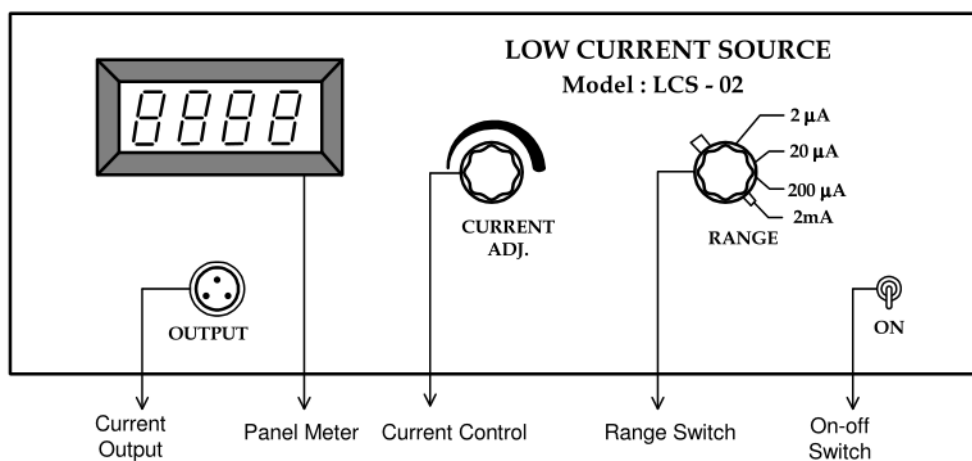
FIG. 2. Constant Current Source, CCS-01
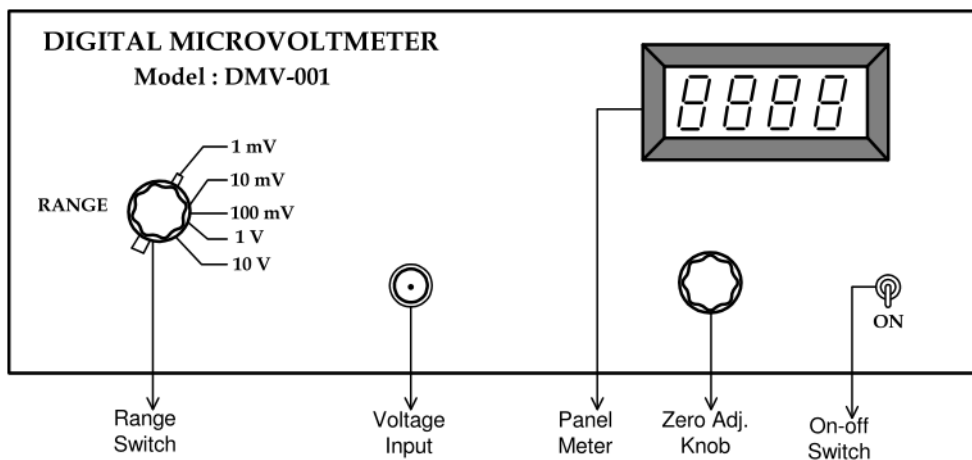


FIG. 3. Low Current Source, LCS-02



FIG. 4. Digitral Microvoltmeter, DMV-001

FIG. 5. Four Probe Arrangement



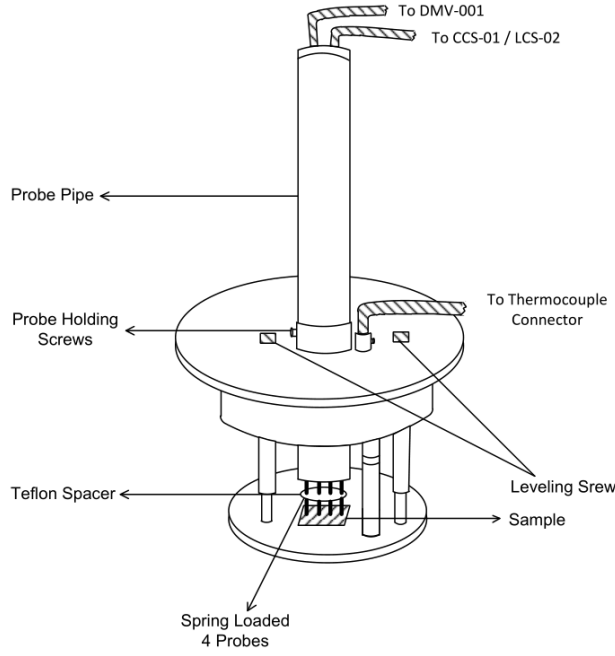FIG. 6. Model for the four probe resistivity measurement



FIG. 7. Circuit used for resistivity measurement

sured across the inner pair. If the flat surface on which the probes rest is adequately large, it may be considered to be a semi-infinite volume. To prevent minority carrier injection and make good contacts, the surface on which the probes rest, maybe mechanically lapped.

The experimental circuit used for measurement is illustrated schematically in figure (7). A nominal value of probe spacing, which has been found satisfactory, is an equal distance of 2.00 mm between adjacent probes.

In order to use four-probe, we assume: the resistivity of the material is uniform in the area of measurement, if there is minority carrier injection into the semiconductor by the current - carrying electrodes, most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible. (This means that the measurements should be made on surface, which has a high recombination rate, such as mechanical by lapped surfaces), the surface on which the probes rest is flat with no surface leakage, the four probes used for resistivity measurements are equally spaced and collinear, the diameter of the contact between the metallic probes and the semiconductor should be small compared to the distance between probes, the surfaces of the material may be either conducting or non-conducting.

### A. Resistivity measurements on a large sample

One added boundary condition is required to treat this case namely, the probes are far from any of the other surfaces of the sample and the sample can thus be considered a semi- infinite volume of uniform resistivity material. Figure (6) shows the geometry of this case.

The floating potential $V_f$ a distance $r$ from an electrode carrying a current $I$ in a material of resistivity $\rho_0$ is given by

$$V_f = \frac{\rho_0 I}{2\pi r} \qquad (1)$$

From here, after some manipulations, we can calculate the resistivity (for the case in figure (6)) as:

$$\rho_0 = \frac{V}{I} - \frac{2\pi}{\left(\dfrac{1}{S_1} + \dfrac{1}{S_3} - \dfrac{1}{S_1 + S_2} - \dfrac{1}{S_2 + S_3}\right)} \qquad (2)$$

When the point spacings are equal, that is, $S_1 = S_2 = S_3 = S$ the above simplifies to:

$$\rho_0 = \frac{V}{I} 2\pi S \qquad (3)$$

### B. Resistivity measurements on a thin slice-conducting bottom surface

Two boundary conditions must be met in this case; the top surface of the slice must be a reflecting (non-conducting) surface and the bottom surface must be an absorbing (conducting) surface. Since the two boundaries are parallel, a solution by the method of images requires for each current source an infinite series of images along a line normal to the plane and passing through the current source.

FIG. 8. The resistivity probes on a slice with conducting bottom surface

The model for this case is shown in figure (8). The side surface of the slice is assumed to be far from the area of measurement and, therefore, only the effect of the bottom surface needs to be considered. In this analysis equal probe spacing $S$ shall be assumed. The width of the slice is $W$. The array of images needed is indicated in figure (8). where the polarity and spacing of the first few images are as shown.

For this case, the resistivity is given by

$$\rho = \frac{\rho}{G_6(W/S)} \quad (4)$$

where $G_6(W/S)$ is a correction term given by

$$G_6\left(\frac{W}{S}\right) = 1 + 4\frac{S}{W}\sum(-1)^n\left[\frac{1}{\sqrt{\left(\frac{S}{W}\right)^2+(2n)^2}} - \frac{1}{\sqrt{\left(2\frac{S}{W}\right)^2+(2n)^2}}\right] \quad (5)$$

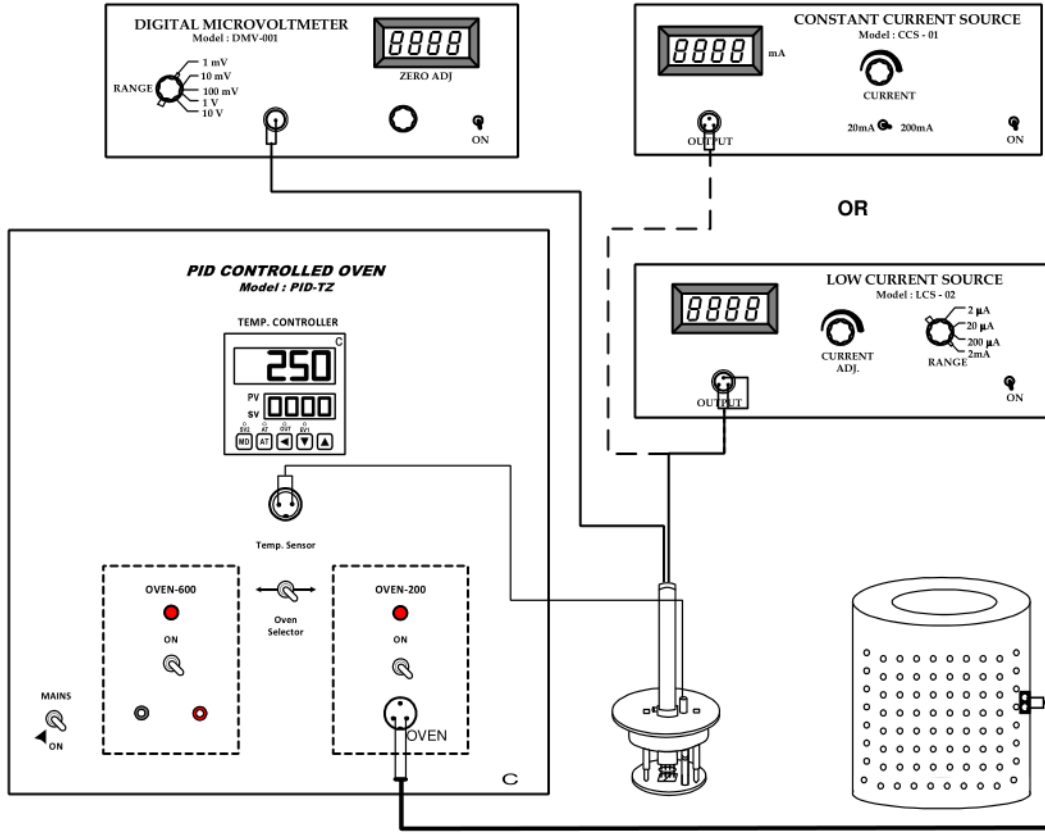## C.  Resistivity measurements on a thin slice-non-conducting bottom surface

The model for these measurements is like the case 2, except that the bottom surface of the slice is nonconducting. This means that all the images of have the same charge as the current source. Then, in this case,

$$\rho = \frac{\rho}{G_7(W/S)} \quad (6)$$

where

$$G_7\left(\frac{W}{S}\right) = 1 + 4\frac{S}{W}\sum\left[\frac{1}{\sqrt{\left(\frac{S}{W}\right)^2+(n)^2}} - \frac{1}{\sqrt{\left(2\frac{S}{W}\right)^2+(2n)^2}}\right] \quad (7)$$

For smaller values of $W/S$, the function $G_7(W/S)$ approaches the case for an infinitely thin slice, or

$$G_7(W/S) = \frac{2S}{W}\ln 2 \quad (8)$$

## D.  Direct and Indirect band-gaps in semiconductors

The band gap represents the minimum energy difference between the top of the valence band and the bottom of the conduction band, However, the top of the valence band and the bottom of the conduction band are not generally at the same value of the electron momentum ($k$). In a direct band gap semiconductor, the top of the valence band and the bottom of the conduction band occur at the same value of momentum ($k$). In an indirect band gap semiconductor, the maximum energy of the valence band occurs at a different value of momentum to the minimum in the conduction band energy.

The difference between the two is most important in optical devices. Each photon of energy $E$ has momentum $p = E/c$, where $c$ is the velocity of light. An optical photon has an energy of the order of $1 \times 10^{-19}$ J, and, since $c = 3 \times 10^8$ m s$^{-1}$, a typical photon has a very small amount of momentum.

A photon of energy $E_g$, where $E_g$ is the band gap energy, can produce an electron-hole pair in a direct band gap semiconductor quite easily, because the electron does not need to be given very much momentum. However, an electron must also undergo a significant change in its momentum for a photon of energy $E_g$ to produce an electron-hole pair in an indirect band gap semiconductor. This is possible, but it requires such an electron to interact not only with the photon to gain energy, but also with a lattice vibration called a phonon in order to either gain or lose momentum.

The indirect process proceeds at a much slower rate, as it requires three entities to intersect in order to proceed: an electron, a photon and a phonon. The same principle applies to recombination of electrons and holes to produce photons. The recombination process is much more efficient for a direct band gap semiconductor than for an indirect band gap semiconductor, where the process must be mediated by a phonon.

As a result of such considerations, gallium arsenide and other direct band gap semiconductors are used to make optical devices such as LEDs and semiconductor lasers, whereas silicon, which is an indirect band gap semiconductor, is not. The table in the next section lists a number of different semiconducting compounds and their band gaps, and it also specifies whether their band gaps are direct or indirect.

A common and simple method for determining whether a band gap is direct or indirect uses absorption spectroscopy. By plotting certain powers of the absorption coefficient against photon energy, one can normally tell both what value the band gap is, and whether or not it is direct.

For a direct band gap, the absorption coefficient $\alpha$ is related to light frequency according to the following formula:

$$\alpha = B(h\nu - E_g)^{1/2} \quad (9)$$

for direct gap semiconductor and

$$\alpha = B(h\nu - E_g)^2 \quad (10)$$

for an indirect gap semiconductor (assuming photon energy is very very less than band gap energy) and $B$ being a constant.

FIG. 9. Connection diagram for the set up



FIG. 10. Complete experimental set up for the four-probe part

## VI. OBSERVATIONS

The current versus voltage readings for n-Al is given in table (I) and is plotted in figure (12). The current versus voltage readings for n-Si is given in table (II) and is plotted in figure (13). The current versus voltage readings for n-Ge is given in table (III) and is plotted in figure (14). The temperature versus voltage readings for Ge wafer at constant current is given in table (IV). The plot between $\ln \rho \sim 1/T$ is plotted in figure (15). The plot between energy and absorption coefficient to the second power for ZnO is given in figure (??) for direct band gap. The plot between energy and the square root of
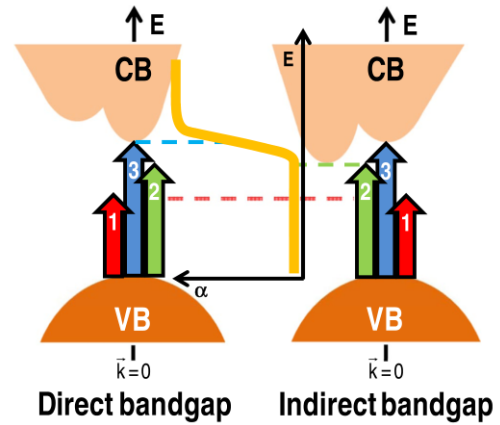


FIG. 11. Simplified energy diagram illustrating the valence (VB) and conduction (CB) bands of direct and indirect band-gap semiconductors.

absorption coefficient for polymer is given in figure (??) for indirect band gap. The following additional observations were made:

1. No. of commercial Al foils: 16

2. Thickness of one foil: 0.001 cm

TABLE I. Readings for calculation of resistivity of Aluminium

| I (mA) | V (mV) |
|--------|--------|
| 0 | 0 |
| 20 | 0.004 |
| 39.5 | 0.01 |
| 59.7 | 0.016 |
| 80.2 | 0.023 |
| 100 | 0.029 |
| 120 | 0.036 |
| 140 | 0.042 |
| 160 | 0.049 |
| 180 | 0.054 |
| 199.4 | 0.061 |

TABLE II. Readings for calculation of resistivity of Silicon

| I (mA) | V (mV) |
|--------|--------|
| 0 | 0 |
| 0.001 | 0.221 |
| 0.002 | 0.313 |
| 0.003 | 0.37 |
| 0.004 | 0.466 |
| 0.005 | 0.616 |
| 0.01 | 1.134 |
| 0.02 | 2.16 |
| 0.03 | 3.21 |
| 0.04 | 4.23 |
| 0.05 | 5.34 |
| 0.06 | 6.4 |
| 0.08 | 8.4 |
| 0.1 | 10.55 |
| 0.2 | 21 |
| 0.3 | 31.4 |
| 0.402 | 42 |
| 0.501 | 52.4 |
| 0.601 | 63 |
| 0.67 | 69.5 |

TABLE III. Readings for calculation of resistivity of Germanium

| I (mA) | V (mV) |
|--------|--------|
| 0.16 | 12 |
| 0.56 | 43 |
| 0.68 | 53 |
| 0.74 | 57 |
| 0.86 | 66 |
| 0.95 | 73 |
| 1.11 | 85 |
| 1.28 | 99 |
| 1.38 | 107 |
| 1.45 | 112 |
| 1.63 | 125 |
| 1.78 | 138 |
| 1.86 | 144 |
| 1.98 | 155 |
| 2.15 | 167 |
| 2.29 | 178 |
| 2.57 | 200 |
| 2.73 | 212 |
| 2.87 | 223 |
| 3.12 | 243 |
| 3.32 | 259 |
| 3.48 | 272 |
| 3.83 | 298 |
| 4.09 | 319 |
| 4.24 | 331 |
| 4.58 | 357 |
| 4.74 | 370 |
| 5.01 | 391 |
| 5.38 | 420 |
| 5.57 | 435 |

TABLE IV. Variation of resistivity of Germanium wafer with temperature at constant current $5\,\mathrm{mA}$

| T (°C) | V (mV) | 1/T ($10^{-3}K^{-1}$) | $\ln\rho$ |
|--------|--------|------------------------|-----------|
| 80 | 0.14 | 2.832 | -1.200 |
| 90 | 0.102 | 2.754 | -1.337 |
| 100 | 0.079 | 2.680 | -1.448 |
| 110 | 0.061 | 2.610 | -1.561 |
| 120 | 0.045 | 2.544 | -1.693 |
| 130 | 0.035 | 2.480 | -1.802 |
| 140 | 0.028 | 2.420 | -1.899 |
| 150 | 0.022 | 2.363 | -2.003 |
| 160 | 0.017 | 2.309 | -2.115 |
| 170 | 0.014 | 2.257 | -2.200 |
| 180 | 0.011 | 2.207 | -2.304 |

3. Thickness of Al Stack: $(0.16 \pm 0.01)\,\mathrm{mm}$

4. Probe distance ($S$): $0.200 \pm 2\%$ cm (fixed)

5. Thickness for n-Si: $0.50 \pm 2\%$ mm

6. Thickness for Ge wafer: $0.50 \pm 2\%$ mm

7. Probe current for Ge wafer: $5\,\mathrm{mA}$ (fixed).

8. Thickness of ZnO: $1\,\mu\mathrm{m}$

9. Thickness of polymer: $150\,\mathrm{nm}$

## VII. CALCULATIONS

We have

$$\rho_0 = \frac{V}{I} 2\pi S \tag{11}$$

And using the correction factor for non-conducting thin-slice case, we have

$$\rho = \frac{\rho_0}{G_7(W/S)} \tag{12}$$

Further, we know

$$E_g = 2k_B \frac{\ln\rho}{1/T} \tag{13}$$
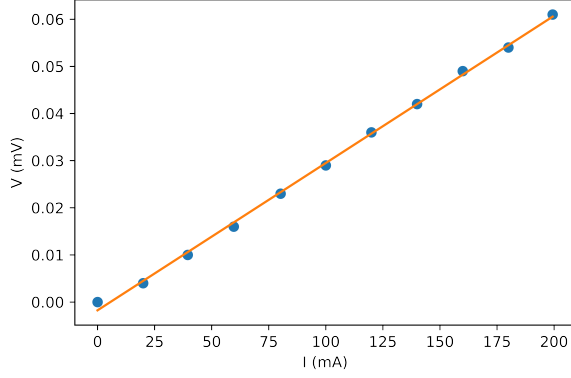
FIG. 12. The $V \sim I$ plot for n-Al
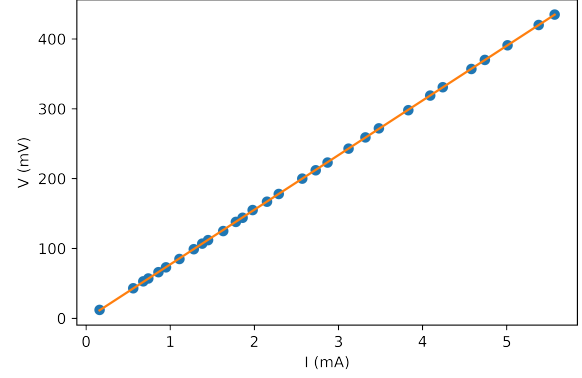


FIG. 14. The $V \sim I$ plot for n-Ge
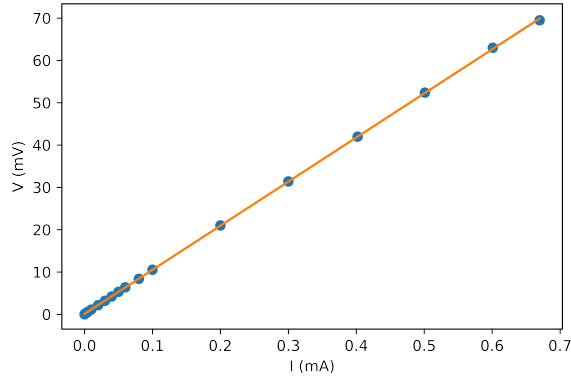


FIG. 13. The $V \sim I$ plot for n-Si
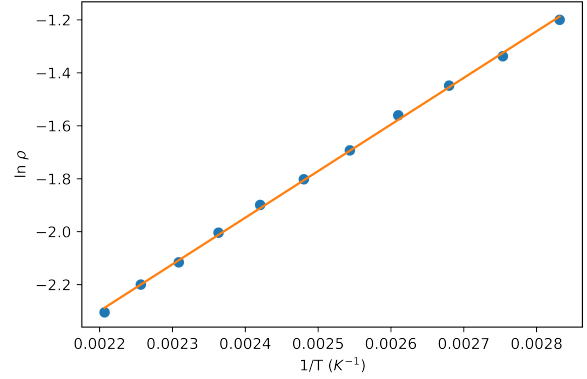


FIG. 15. The $\ln \rho \sim 1/T$ plot for n-Al

where $k_B$ is the Boltzmann's constant, $k_B = 8.6 \times 10^{-5}\,\mathrm{eV}^{\circ -1}$ and $T$ is temperature in Kelvin. We will use the graph of $1/T \sim V$ to find $E_g$.

### A. Resistivity of n-Silicon

From figure (13), the slope of the line is $104.184\,\Omega$. Putting the values in equation (11), we get $\rho_0 = 130.92\,\Omega\,\mathrm{cm}$. The value of $G_7(W/S)$ as calculated from equation (8) is $8\ln 2$. Therefore, using equation (12), we get $\rho_{Si} = 23.60\,\Omega\,\mathrm{cm}$.

### B. Resistivity of n-Germanium

From figure (14), the slope of the line is $78.2644\,\Omega$. Putting the values in equation (11), we get $\rho_0 = 98.35\,\Omega\,\mathrm{cm}$. The value of $G_7(W/S)$ as calculated from equation (8) is $8\ln 2$. Therefore, using equation (12), we get $\rho_{Ge} = 17.74\,\Omega\,\mathrm{cm}$.

### C. The energy band gap of Germanium

From figure (15), the slope of the line is $1760.316\,\mathrm{K}$. Using equation (13), we get $E_g = 0.303\,\mathrm{eV}$. This value is exceptionally different from the expected value and data seems suspect.

### D. The energy band gap of ZnO

From figure (16), the equation of the line (in black) is $y = 181999999999989.4x - 642535999999962.4..$ This line intersects $X$-axis at $x = 3.530\,\mathrm{eV}$ which is the $E_g$ value.

### E. The energy band gaps of polymer

From figure (17), the equation of the lines (in black) is $y_1 = 3395.7079287210813x - 4302.843449537619.$ and $y_2 = 16502.21642362017x - 25774.468514314314..$ These lines intersect $X$-axis at $x_1 = 1.267\,\mathrm{eV}$ and $x_2 = 1.562\,\mathrm{eV}$ respectively which are the $E_g$ values.
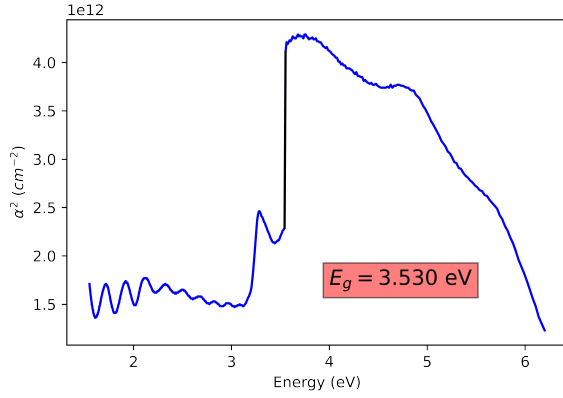
FIG. 16. The energy versus absorption coefficient squared plot for ZnO for determination of direct band gap energy
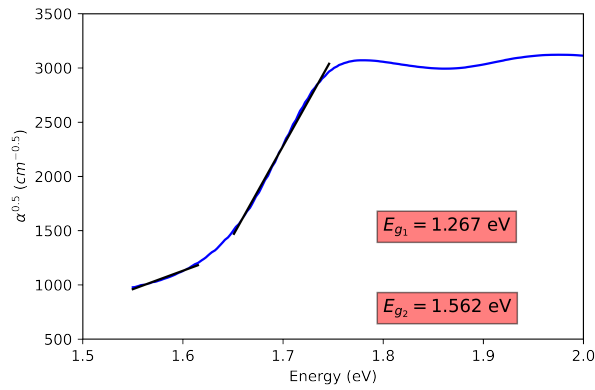


FIG. 17. The energy versus square root of absorption coefficient plot for ZnO for determination of indirect band gap energy

## VIII. ERROR ANALYSIS

The error in resistivity is given by

$$dp = \sqrt{\left(\frac{\partial \rho}{\partial m}\sigma_m\right)^2 + \left(\frac{\partial \rho}{\partial S}\sigma_S\right)^2} \qquad (14)$$

where $m$ is the slope of the $V \sim I$ curve for the semiconductor. Now error in slope, $\sigma_m$ is given by

$$\sigma_m = \sigma_y\sqrt{\frac{s}{\Delta}} \qquad (15)$$

Here $\sigma_y$ is the least count of $V$ and $s$ and $\Delta$ represent the usual summations in regression analysis. For the error in temperature variation of resistivity, the error in $E_g$ is just the error in slope of the graph.

### A. In the resistivity of n-Silicon

Putting the values in the above formulae, we get $d\rho_{Si} = 0.5\,\Omega$ cm.

### B. In the resistivity of n-Germanium

Putting the values in the above formulae, we get $d\rho_{Ge} = 0.3\,\Omega$ cm.

### C. In the energy band gap of Germanium

As the error in $E_g$ is directly given by the error in slope, we can use the equation directly. Upon doing so, we get, $dE_g = 0.003\,$eV.

## IX. RESULTS

1. The resitivity of n-Si is given by $(23.6 \pm 0.5)\,\Omega$ cm which is close to literature value of $24\,\Omega$ cm.

2. The resitivity of n-Ge is given by $(17.7 \pm 0.3)\,\Omega$ cm which is close to literature value of $18\,\Omega$ cm.

3. The energy band gap for Ge is $E_g = (0.303 \pm 0.003)\,$eV which is way off from the literature value of $0.68\,$eV. The possible reasons are discussed in the next section.

4. The energy band gap for ZnO using UV-Vis spectrophotometer is $E_g = 3.530\,$eV.

5. The energy band gaps for polymer using UV-Vis spectrophotometer is $E_{g_1} = 1.267\,$eV and $E_{g_2} = 1.562\,$eV.

## X. DISCUSSIONS

1. The error analysis for the second part of the experiment was not possible because of not enough data points used to calculate the straight line (especially in the case of ZnO).

2. The unusually large error in the value of energy band gap for Ge wafer cannot be explained in any way except for suspect data. The data for Aluminium was also suspects which leads to haywire results.

3. The four-probe method employed in the first part of the experiment to calculate resitivities (and later energy band gap) as several other applications as well like in the field of remote sensing, in production of resistance thermometers in induction hardening process, in the accurate geometry factor estimation and characterization of fuel cells bipolar plates.

## XI. CONCLUSIONS

1. In most cases, the results so obtained were satisfactory.

2. There were few cases where the data appeared suspect which were either left (resistivity of n-Al) or calculated as it is (energy band gap of Ge wafer).