Laboratory Manual

for

MSE 312 Functional Materials Lab

2017-18, II Semester

Department of Materials Science and Engineering
Indian Institute of Technology Kanpur

Instructors: Prof. Monica Katiyar, Email: mk@iitk.ac.in, Ph: 7941

Prof. Anish Upadhyaya, Email: anishu@iitk.ac.in, Ph: 7672

Instructions to the students for MSE-312 laboratory experiments

- Course Schedule MWF: 14:00-17:00
  - Labs will be scheduled on Monday and Wednesday.
  - We will keep Monday for contingency and exams. **DO NOT SCHEDULE OTHER CLASSES IN THAT TIME SLOT.**
- Evaluation: 100%

  Pre Viva (10) + Report of Lab Experiments (30) + Evaluation of daily quiz (20)

  Final Lab exam (Written/Experiment (20), Final Viva (20)

- You must go to the first laboratory session to know about your groups.
- You will be given soft copy of the manual to prepare for pre-viva.
- In all the labs, you MUST come prepared, or else you risk being sent back . Our suggestion is that after you complete an experiment, the same day check out what experiment you have to do the next week and spend 5-10 minutes to take a look at that set-up. This will help you in reading the reference text later.
- Once you lodge yourself by your experiment in the lab, try to understand the set-up, until a laboratory-personnel comes to you to find out how you have planned to do the experiments. If he/she is satisfied with your plan, you can start the experiment. This is part of your preparation.
- Ask TAs any question you like about the set-up; but for technical and theoretical questions, talk to your tutor/instructor.
- For your **safety, come in shoes to the lab**. When you go to your experiment set-up, please **don't fiddle with the instruments**, for if you mess the calibration, it may be difficult for you to finish the experiment in time.
- **THERE WILL BE NO LABORATORY MAKE-UPS**, so make yourself available for all experiments.
- Always keep few lab-sheets and different type of graph sheets (available in the book-stores) with you.
- **For experiments involving data collection, few (3-4) data points will have to be collected and reported in the laboratory report sheet under the observation of a TA, and that TA will sign in front of that data point.**

Lab report

- The report should be written in TECHNICAL ENGLISH, paying proper attention to the language. There are certain styles in technical writing. I will advise you to look up Journal of Applied Physics in the library or internet to understand the meaning of the **headings, such as, introduction, experimental, results, discussion, conclusion**, etc. You must try to understand what kind of content goes under these headings. A guideline is also provided here.
- PAY EXTREME ATTENTION TO HOW GRAPHS ARE PLOTTED. If your plot has to be, for example, Sheet Resistance versus logarithm of Interface Charge, then plot it on a semi-log graph paper. In other words, always keep a supply of linear, semi-log and

log-log graph papers. *Log scale plotted on linear scale after conversion is not acceptable*.

- Also, you will notice the axes of the graphs are labeled with appropriate names and units following them. NO NEED TO LABEL THEM AS X-AXIS and Y-AXIS and then writing the corresponding axis titles somewhere in a corner. Also, don't write things such as "X-Axis: 10 divisions = 15 cm^{-2}". Simply put the appropriate numbers on the graph axes itself.
- In your reports, write your name and the title of the experiment. **No need to fill the report with matters such as theory and experimental set-up; all that is given in your manual.** You should only write on your report the data you take and a nice discussion of what it means. This last part is most important. If you just take data, plot it and do one or two simple curve fitting calculations, it won't earn you much. You MUST discuss what your results mean, where you might have gone wrong, what approximations are inherent in your experiment and calculations and what you have learnt.
- **Individual report must be submitted by each one at the end of lab. (NO GROUP REPORT WILL BE ACCEPTED)**
- You MUST NOT use any sheet other than the one in which you will submit the report. Write all data DIRECTLY on it; any calculation should also be done directly on it. If you **make any mistake in taking data, or calculations, cleanly strike it ONCE and re-write ABOVE the old entry.**
- **USE OF PHONE IS STRICTLY PROHIBITED. (In an urgency go outside from lab)**

Student Guide for Lab Report Presentation

* Details of each heading is provided in the next page

Experiment Number and Name

(i) Aim/ Objective of Experiment

(ii) Results and Observations:
   - a. Which results are being expected (can be bulleted)
   - b. Parametric variables to be used
   - c. Readings taken
   - d. Schematics/ Tables are to be drawn
   - e. Peculiar behavior what you observed can be stated
   - f. Correlation between material, processing , microstructure and properties to be in the record book
   - g. Etc…

(iii) **Discussion: Trying to explain the fundamentals of what you achieved in results** (answering questions of ‘why’ and ‘how’).

(iv) **Conclusions:** based on your results and thorough analysis, you need to conclude.

(v) **References** (on which your methodology, results, or discussions are based)

I hope this commentary on laboratory will help you in organizing yourself in the lab.

For more details on style of report writing you may refer to:

(1)http://www.writing.engr.psu.edu/workbooks/laboratory.html

(2)BASIC COMMUNICATIONSKILLS FOR TECHNOLOGY by RUTHERFOORD, ANDREAJ.(Our library has many copies for this book)

(3) Take a look at journal articles at http://jap.aip.org/forstylesof technical article writing

Note: **Do not forget to get your experimental observations signed by tutor/ TAs.**

Contents of the lab-report

Report **must** be written in the following format

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1. **Aim/ Objective:** Please write what you want to find-out at the end of the experiment
2. **Results and Observations:** First: state your results, and explain the key features of those. Mention those findings or observations in terms of figures, data points, any individual reading etc. Observations could be expressed qualitatively such as in case of colour, smell, cold, warm etc., or quantitatively such as resistance, length, grain-size, temperature etc. Wherever possible, mention your observations quantitatively, i.e. in terms of **numbers** and **units**. It is important that the differences are pointed out clearly in this section (and the reason for those differences must be explained in the discussion section).
3. **Discussion:** Using the figure, image, data-points (in the form of a plot, table,whichever shows the desired trend in a best manner) discuss why any particular observation was made and what such observation indicates. What is the trend of data-points in the plot; **You must draw connection of these observation with the underlying (plausible, if not exact) fundamental science.**
4. **Conclusions:** Finally, based on the observations and discussion, draw conclusions. These are NOT the statement of results, but the outcome (or behavior) if that kind of experiment/ investigation is done.
5. **References:** If you have used conclusions reported by any other investigator inexplaining/supporting your observation/discussions then you mention their work in this last section. If no reference used then write none.

   (See page number of this document for excerpts of a journal article where results of an investigation has been reported)

EXPERIMENT- 1

Ionic Conductivity in Fluorite-Structured Oxides

Aim:

- To measure ionic conductivity as a function of temperature in doped fluorite-structured solids.
- To determine enthalpy for migration of oxygen ions in fluorite oxides.

Background:

Fluorite-structured oxides such as CeO_2 and ZrO_2 have found wide applications in high-temperature energy devices such as solid oxide fuel cells (SOFCs), oxygen transport membrane and chemical sensors. With a relatively large interionic open space, fluorite structure allows for high levels of point defect disorder. A relatively small concentration of point defects ($<10^{20}$ cm^{-3}) may affect the physical properties of these oxides in a very significant ways. For example, ionic conductivity, electronic conductivity, optical absorption, and diffusion can be tailored and modified by the precise control of these zero-dimensional defects. In the present experiment, the ionic conductivity of CeO_2 and ZrO_2 based materials is evaluated as a function of temperature.

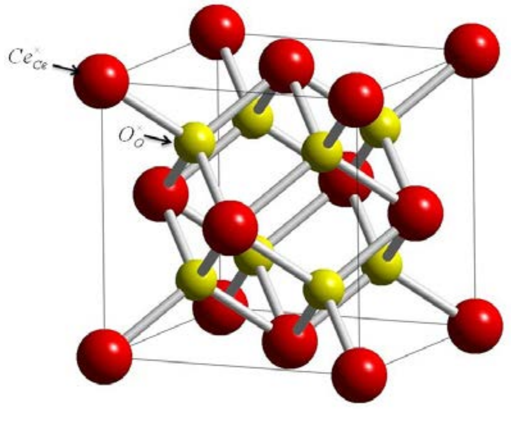
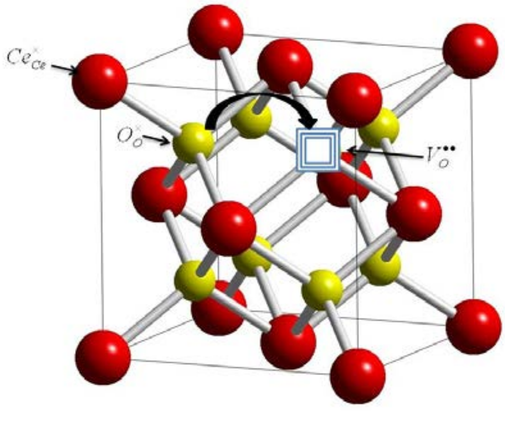
	

Figure 1. Cubic fluorite structure of CeO_2	**Figure 2.** Oxygen ion jump in Gd doped CeO_2

Figure 1 shows the cubic fluorite structure of CeO_2. In this Ce^{4+} cations form the face-centered cubic sub-lattice while O^{2-} anions occupy the tetrahedral positions. There are effectively 4 Ce^{4+}

cations and 8 anions in one unit cell. Thus, there are 4 molecules of CeO_2 in a single unit cell. The co-ordinates of Ce^{4+} and O^{2-} are given as following,

Ce^{4+}: **(0 0 0), (1/2 1/2 0), (0 1/2 1/2), (1/2 0 1/2)**
O^{2-}: **(1/4 1/4 1/4), (3/4 1/4 1/4), (1/4 3/4 1/4), (1/4 1/4 3/4), (3/4 3/4 1/4), (3/4 1/4 3/4), (1/4 3/4 3/4), (3/4 3/4 3/4)**

Typically for fluorite structure oxides, anion Frenkel disorder is a favoured type of intrinsic ionic disorder. Thus, O^{2-} may leave its parent site to occupy the vacant octahedral interstitial positions. The intrinsic disorder reaction can be given as following (in a Kröger Vink notation):

$$O_O^{\times} \rightarrow O_i^{//} + V_O^{\bullet\bullet} \qquad [1]$$

Although these intrinsic ionic defects are present at all temperatures in equilibrium, their concentration decreases considerably on lowering temperature. In fact, oxygen ion conductivity which is a function of concentration of ionic defects and their respective mobility becomes almost negligible at lower temperatures (below 900^{o}C). Thus, oxygen ion conductivity in pure CeO_2 and ZrO_2 is quite poor.

Oxygen ion conduction in these materials takes place via vacancy diffusion mechanism. Thus, an oxygen ion (which is initially occupying the tetrahedral site in the unit cell) can diffuse by moving into an adjacent vacant tetrahedral site of the same kind (see Figure 2). These vacant oxygen ion sites are introduced into the lattice by replacing host cations with acceptor dopant cations. The extrinsic defect reaction when B_2O_3 is doped in AO_2 can be given as,

$$B_2O_3 \xrightarrow{AO_2} 2B_A^{/} + V_O^{\bullet\bullet} + 3O_O^{\times} \qquad [2]$$

Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C). Stabilization of the cubic polymorph of zirconia over wider range of temperatures is accomplished by substitution of some of the Zr^{4+} ions in the crystal lattice with slightly larger ions, e.g., those of Y^{3+}. Substitution of Zr^{4+} ion with Y^{3+} ion creates vacant oxygen ion site.

Diffusion of ion is a thermally activated process and can be given as,

$$D_i = \gamma\lambda^2 \nu [V_O^{\bullet\bullet}] \exp\left(-\frac{\Delta G_m}{kT}\right) \qquad [3]$$

where $[V_O^{\bullet\bullet}]$, γ, λ, ν, ΔG_m, k, and T are the site fraction of oxygen vacancy, orientation factor, jump distance, jump frequency, Gibb's free energy change for migration, Boltzmann's constant and the absolute temperature, respectively. It is important to note that the oxygen ion jumps from one tetrahedral site to another in this material. The ionic conductivity is related to diffusion coefficient as follows,

$$\sigma = \frac{[i]D_i z_i^2 e^2}{kT} = \frac{[i]z_i^2 e^2 \gamma \lambda^2 \nu [V_O^{\bullet\bullet}]}{kT} \exp\left(-\frac{\Delta G_m}{kT}\right)$$
$$= \frac{[i]z_i^2 e^2 \gamma \lambda^2 \nu [V_O^{\bullet\bullet}]}{kT} \exp\left(-\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m}{kT}\right) \quad [4]$$

where z_i, e, ΔS_m and ΔH_m are the charge of ion, columbic charge of electron, entropy change in migration and enthalpy change in migration, respectively. Here [i] is the site fraction of ions related to $[V_O^{\bullet\bullet}]$ as,

$$[V_O^{\bullet\bullet}] + [i] = 1 \quad [5]$$

Thus the equation [4] can be written as,

$$\sigma T = \alpha [V_O^{\bullet\bullet}](1 - [V_O^{\bullet\bullet}]) \exp\left(-\frac{\Delta H_m}{kT}\right) \quad [6]$$

where α is a constant depending upon the dimensions of the unit cell and the entropy change during migration. The equation [6] will eventually takes the following form, which is also termed as Arrhenius relationship for ionic conduction.

$$\sigma T = \sigma_o \exp\left(-\frac{\Delta H_m}{kT}\right) \quad [7]$$

Equation [7] indicates the extrinsic nature of the conductivity in which carrier concentration is fixed by doping, where σ_o is a pre-exponential coefficient given by,

$$\sigma_o = \alpha [V_O^{\bullet\bullet}](1 - [V_O^{\bullet\bullet}]) \quad [8]$$

In the present experiment, student will be given either $Y_{0.148}Zr_{0.852}O_{1.926}$ or $Gd_{0.10}Ce_{0.90}O_{1.95}$. Due to the larger unit cell of ceria than cubic ZrO_2, the ease of oxygen anion diffusion is higher in ceria case (a_{CeO2} = 5.4114 Å and a_{8YSZ} = 5.1339 Å). By measuring the ionic conductivity of an electroded polycrystalline ceramic pellet at various temperatures, student is required to determine ΔH_m and σ_o. Further, using the obtained σ_o and the respective $[V_O^{\bullet\bullet}]$ value in the composition, the value of α needs to be estimated for a given material composition.

Requirements for the experiment:

A. Electrical equipment

1. Tube furnace
2. Sample holder for ionic conductivity measurement. (Schematic of the sampler holder is shown in Figure 3)
3. Dual Digit Measurement Multimeter (GwINSTEK, model-GDM 8261A, 6½ digits)

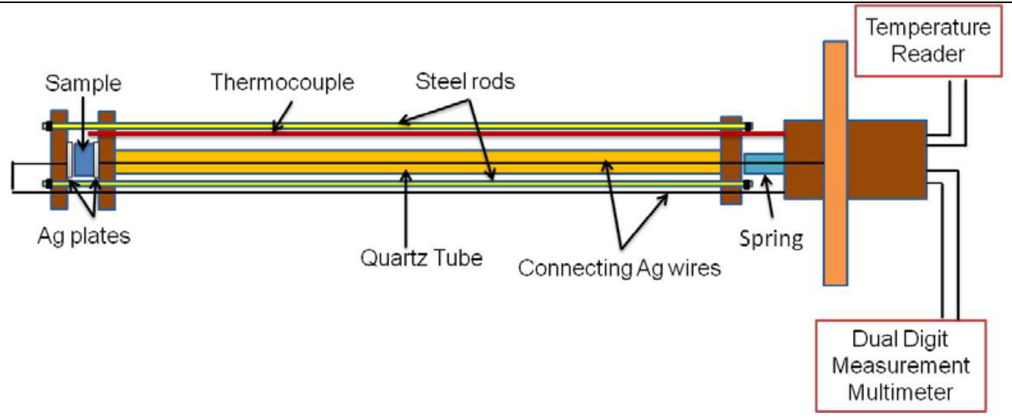


Figure 3. Schematic representation of the sample holder

B. Other requirements

1. Sintered pellets for $Gd_{0.10}Ce_{0.90}O_{1.95}$ (GDC10) or $Y_{0.148}Zr_{0.852}O_{1.926}$ (8YSZ)
2. Silver conductive paste
3. Painting brush
4. Acetone

Brief Description of the Experimental procedure

1. As it takes approx. 1 h to reach 400^{o}C, the temperature of the internal thermocouple inside the tube furnace will be preset to this temperature.
2. The sample holder containing the Ag-electroded cylindrical pellet of either GDC10 or 8YSZ will be already kept inside the tube furnace.
3. It is expected from the student to carefully study the sample holder and draw an equivalent analog electric circuit.
4. The information related to material composition, thickness and diameter of the sintered sample will be provided to the student.
5. Student should connect both the connecting Ag wires coming out from the sample holder to the multimeter and measure the two-probe resistance
6. Once the temperature reading is stable for at least 2 min, measure the temperature of the external thermocouple. At the same time, measure the resistance from the multimeter. The resistance value in the multimeter may fluctuate but student should report an appropriate value at the stable temperature.
7. Manually increase the temperature of the internal thermocouple by 25°C and wait at least for 20 min. for the temperature to get stabilize. Again take the reading from the external thermocouple and multimeter.
8. Continue to take the reading of external thermocouple and multimeter for at least 5 different temperatures.
9. Determine the conductivity (σ) using the geometrical aspect ratio of the sample and the resistance value obtained at a given temperature.
10. Plot log σT versus 1000/T, and estimate the slope by fitting with linear least-square algorithm. From the slope, determine the activation energy (in eV) and σ_o.
11. Using the obtained σ_o value, estimate and report the value of α for a given material composition.

Expectations from the Students:

1. What is the value of $[V_O^{\bullet\bullet}]$ and $[i]$ in GDC10 and 8YSZ?
2. What is the jump distance of oxygen ion during diffusion in fluorite structure oxide?
3. Why 8YSZ exhibits higher activation energy than GDC10?
4. Why do oxygen vacancies (and not cation interstitial or holes) are formed on doping with acceptor oxides?
5. What would be the effect on conductivity of both GDC10 and 8YSZ on changing the environment from air to H_2?

References:

1. D.M. Smythe, "The Defect Chemistry of Metal Oxides", Oxford University Press, 2000.
2. M. W. Barsoum, "Fundamentals of Ceramics" McGraw-Hill, 2000.
3. C. B. Carter and M. G. Norton, "Ceramic Materials: Science & Engineering", Springer 2nd Edition, 2013.

EXPERIMENT-2

Fabrication of Microelectronic Devices

Aim:

Processing of semiconductor devices –special case photolithography of ITO film on glass.

Background:

Processing of semiconductor devices

(The section is taken from a chapter on "Fabrication of Microelectronic Device".[1])

The second part of the last century is known as 'silicon age', and the backbone of this era is precise manufacturing of circuit elements on a single crystal Si wafer. This particular technology of semiconductor processing is known as planar technology and makes possible integration of large number of electronic components on a single wafer [2]. The miniaturization of individual device to make large scale integrated circuits would not have been possible without the advances in processes, techniques and equipments. The availability of cheap electronics today is a testimony to these advances that took place in last 50 years. Advances in microelectronic device fabrication have spun-off new fields like micro-electromechanical-systems (MEMS) [3]. In microelectronic circuits there is no physical displacement between components, while MEMS processing is done to allow physical displacement of components. To a very large extent, today's nanofabrication technology also has its lineage in microelectronics fabrication as many tools developed to work at micro range have been improved and enhanced to provide nano-level observation and manipulation.

If we wish to build a very complicated part, first step is to break it down in various monolithic components, cast or machine them, finally join them using a mechanical or metallurgical joining technique. Microelectronics fabrication is done in such a way that joining between components is done by directly building one component on the other. In other words, joining is at atomic level (nano-scale) between interfaces of two components. The interface itself is a component, e.g. in p-n junction; therefore, we will see later that it is a requirement that we have ultra clean joints between two materials. To attain this precision clean room environment is required for microelectronic fabrication.

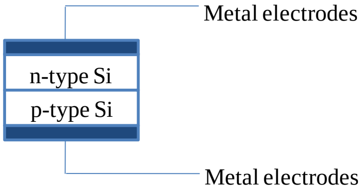


Fig. 1: A p-n diode to be fabricated.

To illustrate the working principle of microelectronic processing, let us see the part in fig. 1 that we wish to fabricate; it is a simple p-n diode in silicon. To this junction, we will make ohmic contacts (means the resistance of the contact is zero) using metal junctions on both sides. In this chapter, all examples are taken from Si technology, because it has most advanced processing technology and it also has large share of integrated circuit market. The processing steps to make this diode are shown in fig. 2.

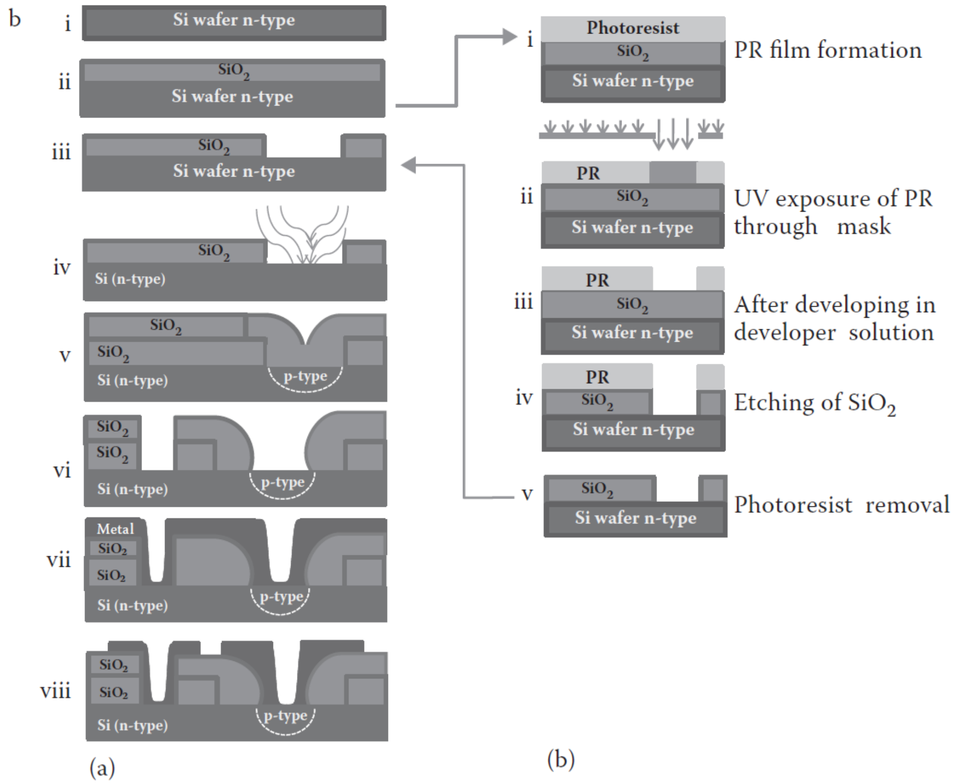


Figure 2.: (a) Processing steps in the fabrication of a p-n junction diode: (i) Single crystal silicon wafer of required doping; (ii) Deposition of a layer of silicon oxide (SiO_2); (iii) Photolithography to open a window; (iv) Introduction of p-type dopant in silicon through the window; (v) Once again, deposition of SiO_2 layer; (vi) Photolithography to open another window; (vii) Metal deposition; (viii) Photolithography to define contacts to p and n region.

Figure 2.: (b) Sub-processes involved in the photolithography step: (i) Spin-coat a photosensitive polymer (photoresist) on the substrate; (ii) Exposure of the coated wafer by UV-light through a patterned mask; (iii) Development of the photoresist; (iv) Etching to remove the undesired part of SiO_2 layer; (v) Remaining photoresist is etched resulting in the desired window in SiO_2 layer.

We start with single crystal silicon wafer of required doping, which is most likely made by pulling a single crystal from a melt and then cut and polished to right size [3]. On this Si wafer, approximately 500 microns thick and anywhere between 50-300 mm in diameter, first we deposit a layer of silicon oxide (SiO_2); this is generally done by thermal oxidation or chemical vapor deposition (CVD). The thickness of this layer is decided by the requirement of the subsequent processes. A window is opened in the oxide. This process is called photolithography and is subdivided into many sub-processes as shown in fig. 2(b). In photolithography, we spin-coat a photosensitive polymer (photoresist) on the substrate. Typically we bake the wafer before and after spin coating (pre-bake and post-bake). This is followed by exposure of the coated wafer by UV-light. However, the photoresist experiences exposure to UV light only in the desired areas because it is protected by a patterned mask (for example, a glass plate on which chromium is coated in a pattern, preventing the UV light to pass through). Following development of the photoresist, the surface that needs to be removed is exposed and the one we need to retain is protected by PR, we use an etching agent that will remove the undesired part of SiO_2. Finally PR is also etched away from top of the layer and we get the net shape desired on the SiO_2. In the next step, p-type dopant is introduced in silicon through the window using diffusion or ion implantation process. The thickness of the masking oxide should be enough to ensure that dopants are not introduced in the covered portion of silicon wafer. The p-n junction is created by this process. Once again we deposit SiO_2 layer; next we open two windows in this as shown in (vi) using previously explained photolithography process. Thin film of metal electrode is deposited (sometime additional processing may be needed to ensure ohmic contact) to make contact to n and p portion of the Si wafer. The metal film will again need to be patterned using photolithography. Now the device is ready, in practice another passivating layer is deposited and patterned to protect the devices. The final device in fig. 2 may not look the same as in fig 1 from geometry point of view, but it has exactly same electrical characteristics. For microelectronics that is the important part, not the physical appearance. Another interesting thing in this transformation of the component shape is that we can take both contacts from top of the surface, this makes integration very easy. In integrated circuits, millions of such devices need to be fabricated and connected on a single wafer. All fabrications steps are in a single plane – hence it is called ‘planar technology’. After chip fabrication, it is tested, wire-bonded, and packaged; these are also very important parts of microelectronics fabrication.

Power of large scale integration in microelectronics - We have briefly seen processes in making a discrete device on silicon, but power of planar technology is in the capability to integrate large number of discrete devices (transistors, capacitors, resistors, etc) to make circuits on a silicon wafer. Also the starting size of silicon wafer has also increased from being approximately 2” to 12” on which large number of such circuits can be fabricated simultaneously. The scoring point about manufacturing is that yield is sufficiently high to reduce the cost of single chip. There are many factors that contribute to the success of semiconductor manufacturing technology:

1. Cleanliness during manufacturing is critical to maintain low contamination of surface. Therefore, clean rooms are must for good process control and high yield in manufacturing.

2. The development of process technology to allow integration of even larger number of devices every year. Moore (fig. 3) predicted this advancement in 1970 and his prophecy has been fulfilled.

3. Use of automation in the microelectronics fabrication facilities (fabs) to improve yield.

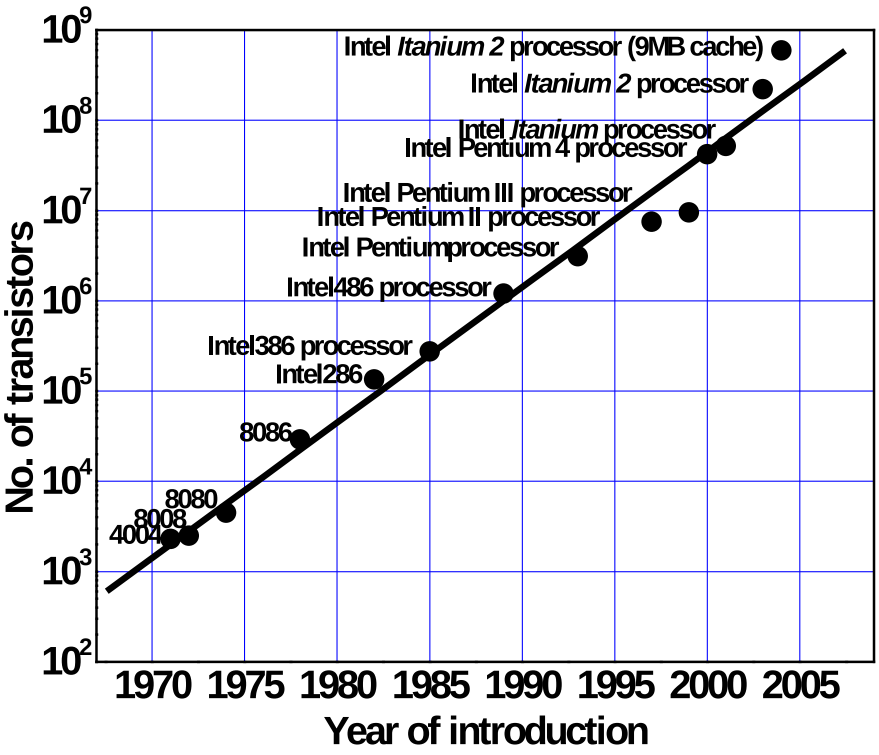


Figure 3: Moore's law for microprocessors – showing exponential increase in number of devices for an application.

In summary, we have created a component by adding the material and patterning it. The two processes that add a new material to an existing component are thin film deposition and diffusion/ion-implantation (this modifies the existing material). Processes that pattern the components are photolithography and etching.

It is not possible to fabricate an inorganic semiconductor device in the teaching lab at present, but we can attempt to make an organic semiconductor device. This is because organic semiconductors can be solution processed and do not require costly equipments. Therefore, objective of the next experiment is to fabricate organic photovoltaic cells. In this experiment we cover photolithography.

Requirements for the experiment:

Materials:

1) PR Solution (Photo resist)
2) ITO coated for patterning
3) Rubilith Mask
4) KOH Solution (Developer)
5) ITO Etching Solution
6) DI water, acetone.

Equipment:

1) Sample holder
2) Ultrasonicator

3) Multimeter
4) Spin coater
5) Hot plate or oven

Other requirement:

Beakers, Spatula, Tweezers, Syringe, Al foil, Petridish, Apron, Gloves, Mask, Head Cover, Eye Glasses

Brief Description of the Experimental Procedure

Basic Fabrication Steps:

1. Cleaning of ITO coated glass substrate
2. Photolithography

1. Cleaning of ITO coated glass substrates:

1. Wear safety equipments (apron, gloves, mask, head cover, eye glasses).
2. Wash the equipments beakers, syringes, petridish, stand, twizzer and measuring cylinders with once with soap solution and thrice with DI water respectively. Put them in oven at 110^0C. CHECK: This step may already have been performed before you come to the laboratory.
3. Turn ON the clean bench, if it is not already turned ON. Switch on the air blower from the switch located in front panel of the clean bench.
4. Check which side of substrate is conductive. Conductive side is ITO (anode). Then mark the glass side, some number so that we can easily recognize the ITO side.
5. Wash patterned ITO substrates in soap solution with the help of a tooth brush and rinse them first in tap water and then in DI water. Place all the substrates in Teflon sample holder (figure 2).

Figure 4: Washing Substrate with soap and DI water

Figure 5: Placing of substrates in Teflon sample holder

6. Clean these substrates using ultrasonicating them in DI water, acetone. Make sure that substrate should be completely dipped in acetone. Put that beaker in ultrasonicator which should be on the clean bench. ATTENTION: water should be filled 2/3 of the height of ultrasonicator. Switch on the ultrasonicator by on/off button and set timer for ultrasonication. We can increase/decrease the time in the step of 5 minutes by pressing arrow up/ down button. Here we do ultrasonication for 10 minutes (figure 3 a and b).

Figure 6: **(a)** substrates placed in ultrasonicator **(b)** magnified view of front panal from where we can set time and temperature for ultrasonication.

7. Repeat step 6 for methanol and DI water. Dry the substrates by holding it with tweezer using drier. Keep these substrates in a petridish and place them in oven at a temperature slightly above 100^0C (approximately 110^0C) for 10 min, to evaporate any residual water.

8 Take out the substrates out of oven and let them cool before proceeding to the next step.

2. Photolithography

1. Cover the spin coater with Al foil. (adjusted in above step)
2. Preparation of developer solution: TMAH. (adjusted)
   Preparation of ITO etching solution: Nitric acid, HNO_3:HCL:DI water :: 1: 4:15 at a temperature of 55^oC . (adjusted)
3. Set hot plate temperature at 120^oC.
4. Take out the substrates and place them in yellow room for 5 min. to cool down at room temp.
5. Spin coat PR at 3000 rpm for 30 second.

Figure 7: PR Coating using Spin Coater

6. Prebake substrates at 120^oC for 5 min on hot plate.
7. After prebake set hot plate temperature 140^oC.
8. Align the Rubilith mask on the substrate (ITO side up) and keep it under UV light for 1 minutes and 20 second in local UV lamp .
9. Develop using developer solution (TMAH) by keeping substrates in for 55 sec.
10. Dip substrates in DI water for about 30 sec.
11. Dry the substrates.
12. Post bake the substrates at 140^oC for 10 min.

13. Remove the PR from edges and other unwanted places.
14. Dip the substrates in ITO etching solution (at temperature 70^{o}C) for about 5 minute, rinse in DI water and after drying one substrate check for ITO patterning using multimeter.
15. After etching, remove PR by dipping substrates in acetone or wipe it using a clean cloth.
16. Check connectivity of ITO.

Expectations from the Students:

1. Hands-on experience in device processing of an organic solar cell
2. Draw the side and top view of you sample at each step of fabrication.
3. Report Resistance of Patterns with the help of multimeter
4. IV slop of patterns made on ITO coated glass
5. Calculate sheet resistance with the help of formula given below

$$R = \rho\, l/A,$$

ρ; Resistivity

l; length of ITO pattern

where, A; t * w

t; thickness of ITO layer

w; width of pattern

6. Discuss the effect of exposure time on pattern.
7. List all the processing parameters, at each step, that can affect the process of photolithography. Explain.

References:

1. Deepak, Vikram Verma, Monica Katiyar , Fabrication of Microelectronic Devices in Micromanufacturing Processes edited by V.K. Jain.
2. Andrew S. Grove. 1967. *Physics and technology of semiconductor devices*. John Wiley and Sons, Singapore
3. S.M. Sze. 1994. *Semiconductor Sensors*. John Wiley & Sons, Inc., New York.

EXPERIMENT - 3

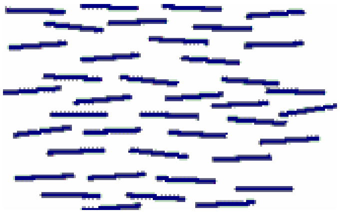
Electrical and optical properties of Liquid Crystals

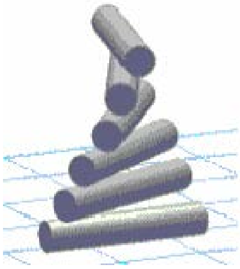
Aim: To measure electrical and optical properties of liquid crystals

Introduction/Theory:

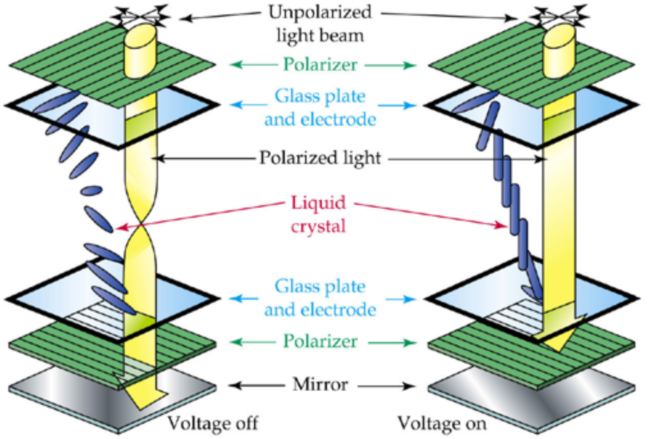
Liquid crystals are used in wide range of applications, the main and more common application being liquid crystal displays (or LCDs). Most of the flat panel displays are LCDs. Liquid crystals, have an intermediate phase between a crystalline solid phase and an isotropic liquid phase and hence are termed as the liquid crystalline phase. This phase is also known as mesomorphic phase or mesophase. The materials which exhibit this phase are then called liquid crystals, mesomorphic substances or mesomorphs.

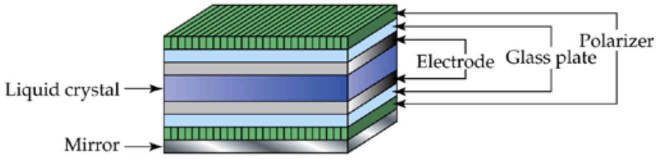
Liquid crystal molecules have shape anisotropy and are mostly made up of rod-like molecules. In liquid crystalline phase these molecules exhibit orientational order. Depending on the molecular arrangement, liquid crystals can be divided into four main categories: (i) nematic liquid crystals, (ii) cholestic liquid crystals, (iii) smectic liquid crystals and (iv) columnar liquid crystals. Of these nematic liquid crystals are of particular importance for liquid crystal displays.





The image on the left shows molecular order of rod-shaped molecules in nematic liquid crystal. A twisted nematic liquid crystal (TNLC) display cell is made by sandwiching a layer of liquid crystal molecules between two glass plates. The molecules of liquid crystal material are oriented parallel to glass surface, but the top and bottom glass plates are oriented such that at two glass surfaces, the orientation of molecules is perpendicular to each other as shown in figure on right.



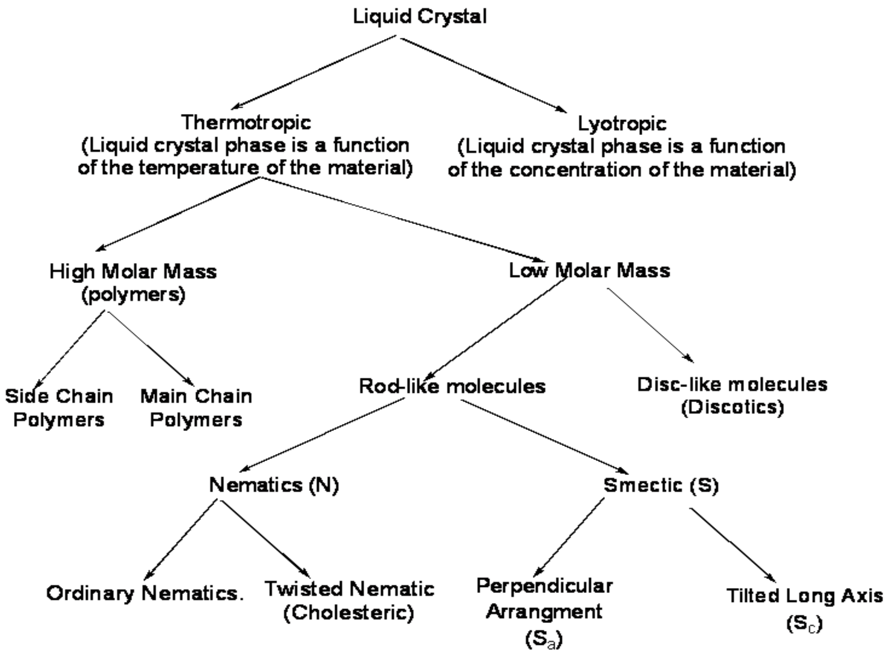


To make a complete cell, this liquid crystal glass is placed between two polarizers with polarization direction perpendicular to each other and a light source at one end. Schematic of a display cell and its principle of operation is shown in the figure on right.

When unpolarized light beam passes through first polarizer, it gets linearly polarized. The twisted nematic liquid crystal molecules act as a waveguide and change the polarization of the light by 90° such that light can pass through the second polarizer which is perpendicular to first polarizer. Hence, in the "off" mode the display cell appears to be transparent (or bright) when placed between two perpendicular polarizers. When a certain voltage is applied, the molecules in liquid crystal lose their orientation and get oriented in the direction of electric field, due to positive dielectric anisotropy (the difference between dielectric constants in direction parallel and perpendicular to molecule axis). In this "on" state the liquid crystal molecules do not act as a waveguide and the linearly polarized light cannot pass through the polarizer (with polarization direction perpendicular to the light beam) and the display cell appears opaque (or dark). Thus by applying a certain voltage the cell can be made to appear bright (transparent) or dark (opaque), while the backlight (the light source) remains on.

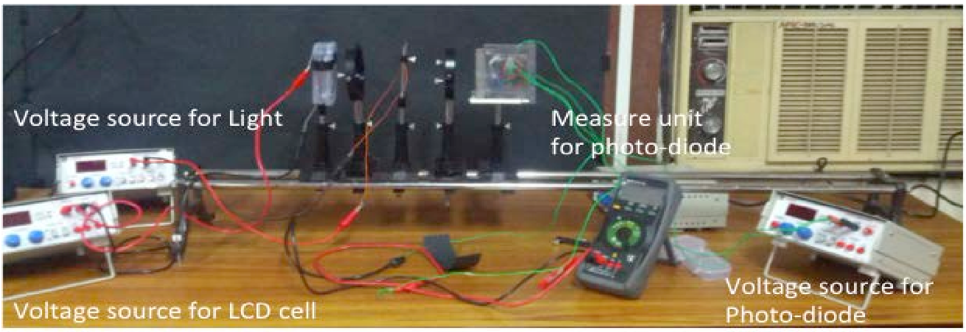
In a color LCD display, a pixel is made of three display cells each with either red, green or blue color light (using color filters). Thus, the color of each pixel can be controlled, by controlling how much light passes through each sub-pixel (red, green or blue), which in turn depends on the voltage applied on the display cell. A very large number of such pixels with independent color control form a display. The voltage on each display cell can either be controlled by a grid (row and column) of electrodes as in passive matrix liquid crystal displays (PMLCD) or by a transistor at each sub-pixel as in active matrix liquid crystal display (AMLCD). Most of the displays that you come across in your daily life (such as computer/laptop screens, mobile/tablet screens etc.) are active matrix LCD.

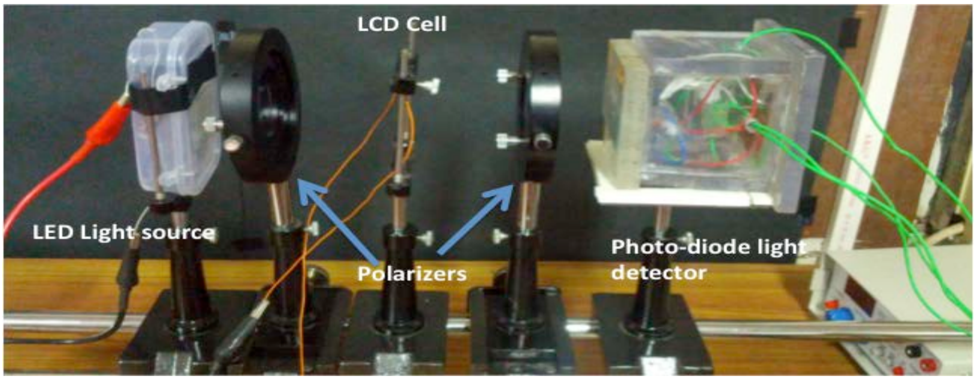
Classification of Liquid Crystals:

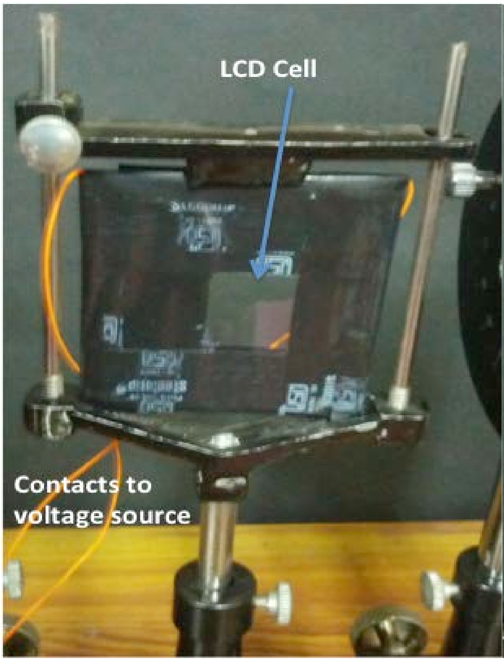


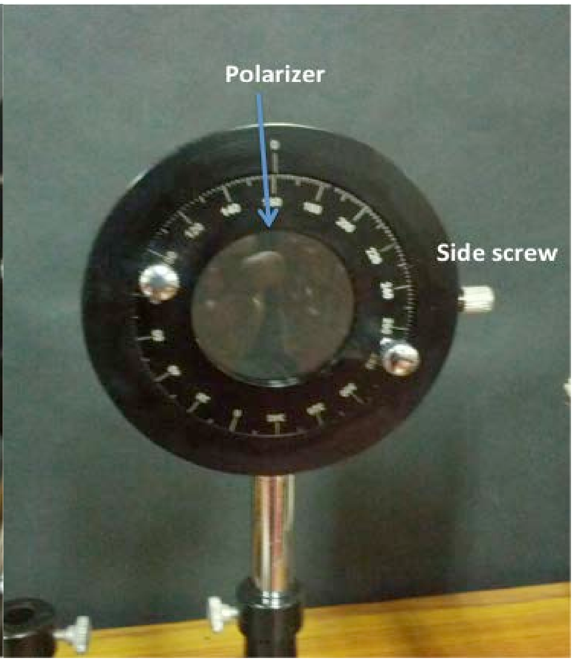
Methodology:

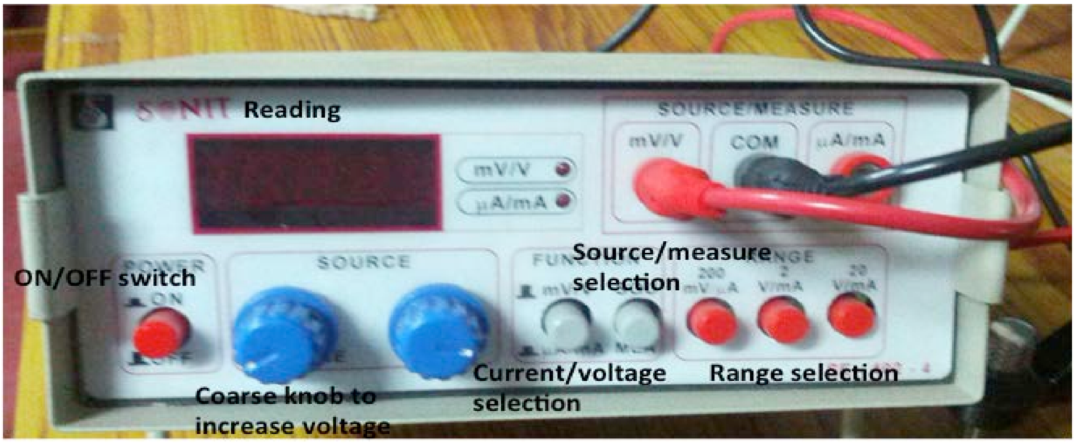
In this experiment, you would measure the transparency of various optical elements, such as polarizers and liquid crystal display cell by means of measuring response of a photo-diode in presence of light. The picture below shows the experimental setup, with some of the components enlarged for clarity.











Steps involves in experimental procedure:

1. Make sure all power sources are off.
2. Remove (gently) both polarizers and LCD cell from the holders and place on table. (take extra care while removing LCD cell, as it is attached to a voltage source)
3. Turn on voltage sources for light source (9.0 volts) and photo-diode (15.0 volts). Turn on the measure unit for photo-diode (a multi-meter). Wait 30 seconds for it to stabilize and take a reading (take notice of the units). This is the light falling on detector when there is no optical element in between light source and detector (photo-diode). [*For a more reasonable reading cover your set-up with a black sheet to exclude ambient light*.]
4. Turn off the light source and take a reading. This should be your dark response from the photo-diode.
5. Now carefully put the first polarizer in the holder (with side-screw on polarizer facing you). First polarizer is the polarizer closer to the light source. Make sure polarizer surface is perpendicular to optical path. Tighten the holder screw to make sure that it does not rotate. Make sure that first polarizer is set to 0 position. Take a reading from measure-unit (multi-meter) to see how much light is falling on the detector. Compare this value to the previous reading. Is there a difference? Why? [*For a more reasonable reading cover your set-up with a black sheet to exclude ambient light*.]
6. Now carefully put the second polarizer in its holder and tighten the holder screw (closer to detector, make sure the side-screw is facing you). Loosen the side-screw on polarizer and rotate the polarizer to minimize the reading on measure unit. Note down this reading and polarizer rotation and tighten the side screw. Why do we minimize this reading? What do you infer about two polarizer positions from this? [*For a more reasonable reading cover your set-up with a black sheet to exclude ambient light*.]
7. Now, insert a third polarizer in optical path between the first two polarizers. Rotate this polarizer and observe the change in reading on measure unit. What do you observe and how would you explain this behavior? Remove this polarizer.

8. Now gently put the LCD cell in the clip holder between two polarizers (without disturbing the electrical connection). Make sure that cell surface is perpendicular to optical path. Take a reading again from the measure unit and explain the difference. [*For a more reasonable reading cover your set-up with a black sheet to exclude ambient light*.]
9. Now turn on the voltage source attached to the LCD cell. Make sure that "source/measure" button is in depressed mode and the voltage range is in 20 volts. Using the coarse knob, increase the voltage in interval of 0.5 volts at a time and take a reading from measure unit (for every reading, wait for 30 seconds for it to stabilize).Turn the knob slowly to increase voltage to LCD cell (you need less than a quarter turn to increase voltage by 0.5 volts).[*For a more reasonable reading cover your set-up with a black sheet to exclude ambient light*.]
10. Take readings upto 10 volts. Plot a curve with applied voltage (to LCD cell) as x-axis and the reading from measure unit on y-axis. Explain your observations.
11. While at 10 volts, turn of the voltage to LCD cell by turning off the voltage source (Not from knob). Take a reading from measure unit.
12. Now rotate the coarse-knob of LCD voltage source in anti-clock direction all the way (with voltage source turned off). Turn on the voltage source and repeat steps 8, 9 and 10.
13. Write a paragraph explaining all the results that you have obtained and the reasons for these results. In case your results are not what you expected, explain what could be the reason for these un-expected results.

Note: *Wait for 30 seconds for the reading on measure-unit (multi-meter) to stabilize before taking a reading. Keep your set-up covered for measurements.*

Expectations from students:

1. Learn about liquid crystal materials and their importance
2. Learn polarization of light
3. Learn about various optical elements – such as, light source, polarizers, LCD cell, detector etc.
4. Learn voltage response of the liquid crystals
5. Measure and plot the voltage response of LCD cell and determine the threshold voltage.

EXPERIMENT - 4

Fabrication and Characterization of Organic Light Emitting Diodes

Aim:

i) Fabrication of an organic light emitting diode (OLED) and observation of light output

ii) I-V characterization and calculation of turn-on voltage from the I-V plot

iii) Measurement of electroluminescence and calculation of band gap from EL plot

Background:

Till a decade ago, the semiconductors that were found in nearly all electronic device applications were all inorganic, silicon, germanium, gallium arsenide, gallium nitride etc. Simultaneously, the term organics as a form of engineering material evoked the thought of electrical insulators. But, a new field of electronics has emerged with the discovery of conducting and semiconducting organic materials in solid forms.

Among the organic materials for electronic applications, we are mostly interested in that class which contains π-electrons. For example, the sp^2 hybridized carbon forms three co-planar π-bonds; for example, in C_2H_4, the carbon atom bonds with the other carbon and two hydrogen atoms. The fourth orbital (p_z) is perpendicular to the sp^2 hybridized orbital plane and leads to additional π bonding between the two carbon atoms. The molecular orbitals thus formed split into bonding and anti-bonding states, which commonly are also known as **HOMO (highest occupied molecular orbital) and LUMO (lowest un-occupied molecular orbital),** respectively (see Fig. 1).These molecules form solids via a weak intermolecular bonding, clubbed together under the name of “van-der waals bonds”. On account of this weak bonding and disorder in the structure, although the HOMO and LUMO levels may take shape of an energy band, the bands are rather narrow. Furthermore, consequence of this weak intermolecular bonding is that the electronic properties of the organic solids are largely determined by the molecules themselves; role of the weak forces is mostly to hold the organic molecules together in a solid.

Further understanding of organic semiconductors may be gained by comparing them with common inorganic crystalline semiconductors held together by covalent or ionic bonds. Because of periodicity of the lattice, a description of electronic states in reciprocal space, k, is possible in these materials. Correspondingly, an inorganic semiconductor has an occupied valence band separated by an empty conduction band, as shown in Fig. 2. In that sense, an analogy between valence band and HOMO level and conduction band and LUMO is possible. But, the width of the energy bands in inorganic semiconductors is much larger, which has a consequence on the mechanism of the charge transport.

Comparison of organic and inorganic semiconductors: The properties of the two types of semiconductors are compared in **Table 1**, which also indicates applications that will be possible with organic semiconductors. Apart from differences in bonding, the electrons and holes are the free carriers in inorganic semiconductors, whereas the organic semiconductors generally do not support free electrons and holes. The corresponding charge carriers in organic semiconductors are a positive or negative polaron.

Furthermore, in inorganic semiconductors, the positive and negative charges form excitons (Wannier- Mott type) with small binding energies; thus excitons are rarely observed at room temperature in common semiconductors. In contrast, organic semiconductors demonstrate large binding energies for excitons (Frenkel type) and hence they play a major role in determining the optical behavior of the organic semiconductors.

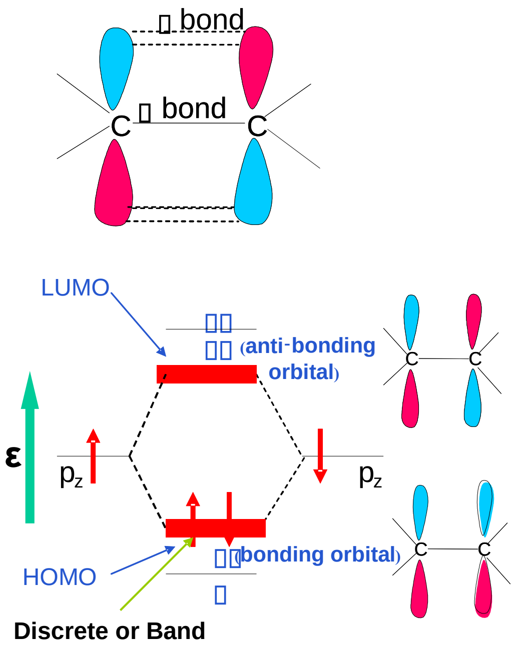


Figure 1: Ethylene molecule with σ and π bonds. Molecular bonding leads to bonding (occupied) and anti-bonding (empty) states, both corresponding to σ and π bonding orbitals. In solid form, the resulting HOMO and LUMO states take a form of bands, analogous to crystalline semiconductors, but the band-widths are significantly smaller.

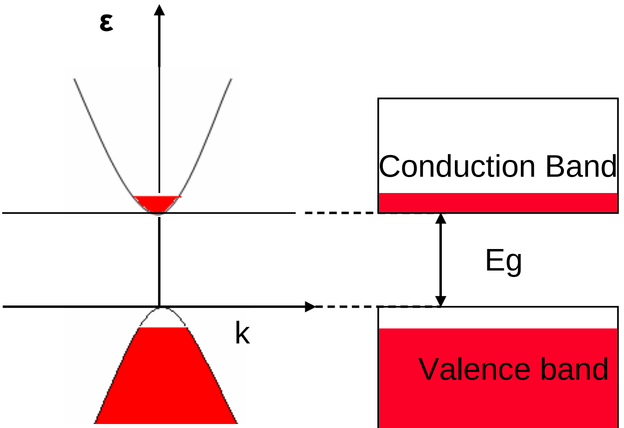


Figure 2: Valence and conduction band in crystalline semiconductors. The valence band is completely occupied by electrons and conduction band is empty at 0K. At higher temperatures, some electrons

from the valence band populate the
conduction band.

Table 1: Comparison of molecular/organic with crystalline/inorganic solids

	Crystalline/ Inorganic solid	**Molecular/ Organic solids**
Bonding	Ionic, Covalent, Metallic (2-4ev)	Ionic or covalent within molecule (intramolecular), but the solid is held together by Van-der Waal force (0.01 eV). Therefore, solid's behavior to a large extent governed by individual molecules and increased vibrational modes
Charge Carrier	Electrons, holes, ions	Polarons, exciton (though neutral)
Transport	Band	Hopping
Mobility	10^2-10^4 cm^2/Vs	10^{-6}-1 cm^2/Vs
Exciton	Wannier- Mott	Frenkel, Charge transfer
Luminescence	Band to band recombination (at practical temperature)	Exciton recombination

In context of charge transport, the mobility of carriers in organic semiconductors is small in comparison to that in inorganic crystalline semiconductors. This mobility of charge in organic semiconductors is defined by a hopping mechanism for transport, unlike band transport in inorganic semiconductors.

Applications of Organic Electronics: Comparison with inorganic crystalline semiconductor reveals that mobility of carriers in organic semiconductors is limited to 1 cm^2/Vs (generally positive charge carriers are more mobile), two or three order of magnitude lower than that in conventional semiconductors. Therefore, applications addressed by these materials are also which do not require too high mobilities. Such applications can broadly be classified into those where only the charge transport is important, such as organic thin film transistors because organic semiconductors can perform equivalent to amorphous silicon, or where optical properties are more important, such as in solar cells, solid state lighting source or organic light emitting diode (OLED) based displays. In the latter set of applications, the charge transport is not as important as the balance of electron and hole like conduction in a device and absorption/emission of photons. Among these, the OLED displays are in the most advanced stage, already appearing in commercial domain, for example, as in displays in high end mobile phones.

Development of OLEDs: The excitement in this field started with a Nobel Prize in 2000 in chemistry awarded to Alan G. MacDiarmid, Hideki Shirakawa and Alan J. Heeger for discovery of conducting polymers. This discovery in itself is important that it established that certain polymers known to be insulators or semiconductors, when electrochemically doped could show very high conductivity [1]. For example, polyaniline or trans-poly acetylene having conductivities 10^{-10} and 10^{-5} S/cm, respectively, when electrochemically doped could show conductivities as high as 10^3 and 10^5 S/cm, respectively [2]. This conductivity is very close to that of conducting metals such as copper. However, while the impact of this scientific discovery was enormous, practical use of such polymers has been limited thus far.

With respect to the engineering achievements, especially with OLED, focus has mostly been on un-doped form of these polymers or even small organic molecules. The conductivity in these semiconducting materials exhibiting a "band-gap" is much lower, but the devices are engineered for short transport distances to keep the transport problem arising from low conductivity manageable. Simultaneously, we exploit the optical properties arising from the presence of "band gap". [Note: With a myriad of organic materials possible, "band-gap" selection is much easier than in conventional single crystal inorganic semiconductors, limited on only a handful of materials.]

In a letter in 1962, Pope et al. [3] demonstrated faint electroluminescence from anthracene crystals, 10-20 mm thick. But applied voltage was as high as 400V. The problem was a combined effect of poor conductivity accompanied by large thicknesses leading to excessive resistance in the device. Furthermore, imbalance between mobility of the positive and negative charges carriers ensured dominant recombination near the cathode leading to non-radiative recombination. It took several decades before borrowing from the ideas behind conventional heterostructure LEDs, first practical OLED was built by Tang and Van Slyke [4] in 1987 which yielded measurable light emission at voltages less than 10 V. In most organic materials, the hole mobility is at least 10-100 times greater than that of an electron. Thus, the bilayer OLED that blocked the holes at the interface of the two organic materials, moved the recombination zone away from the cathode and improve charge balance, leading to a better efficiency device. But, the OLED, reported in [4] emitted in green; the displays require three primary colors, usually red, blue and green. Another report from the same group [5] in 1989 included dopants in a host, allowing for energy transfer from the latter to the dopant molecules. This allowed modulation of colors in the same device.

The emission from these devices was fluorescent. That meant, even the ideal electroluminescent quantum (internal) efficiency could not be more than 25%, especially in OLEDs fabricated with small organic molecules. In this regard, another development in late 1990 is noteworthy. Forrest's group [6] succeeded in harvesting the triplet excitons, taking the quantum efficiencies to nearly 100% with Ir-complexes based phosphorescent devices [7]. In the context of displays, more important was the time constant of triplet emission, in microsecond range. An advantage of an OLED display over the liquid crystal display (LCD) is that the former can display fast moving images much better owing to their faster response speed, typically microsecond in OLEDs and millisecond in LCDs. Phosphorescence is usually associated with slow emission, but a fast emission in the Ir-complex based devices preserved the advantage of the OLED devices.

The OLED devices are made from two types of organic materials - the first are called small molecules and the other polymers. The early development of OLED occurred with small molecules, whose thin films are obtained by thermal evaporation, and other processes which are well established in micro-electronics. In early to mid 1990's, Friend and his co-workers [8] demonstrated OLED devices based on polymers, with very different processing methods. Since, most polymers are difficult to thermally evaporate, but can be made soluble in many volatile solvents, it became possible to spin-coat the polymer thin films required in an OLED. This option of solution processing, by spin coating or ink-jet printing, opens up potentially a much cheaper route for fabricating OLEDs. However, lack in pace of development of required equipment, and easy availability of equipment/process for small molecules, early commercialization of OLED displays has been through small molecule organic materials. Nonetheless, a few small sized monochrome displays based on polymers did become available commercially.

For details of major industrial landmarks that have led to commercialization of OLED displays, refer to the **web-site: http://www.oled-info.com/history**.

Basics of OLED technology: An OLED, as shown in **Fig. 3**, consists of multiple organic layers sandwiched between two electrodes marked as cathode and a transparent anode, typically made up of indium tin oxide (ITO). Each organic layer has a specific function, with a total thickness all organic layers on the order of 100 nm. When electrons and holes are injected into this device from their respective electrode, the structure in **Fig. 4** is so engineered that the two types of charges meet up in the emissive layer. Here they form an exciton, which upon relaxing emits light corresponding to the nature of the emissive layer. This process just described is shown in a band diagram in Fig. 4 consisting of HOMO and LUMO levels of organic material in alignment with work functions of anode and cathode.

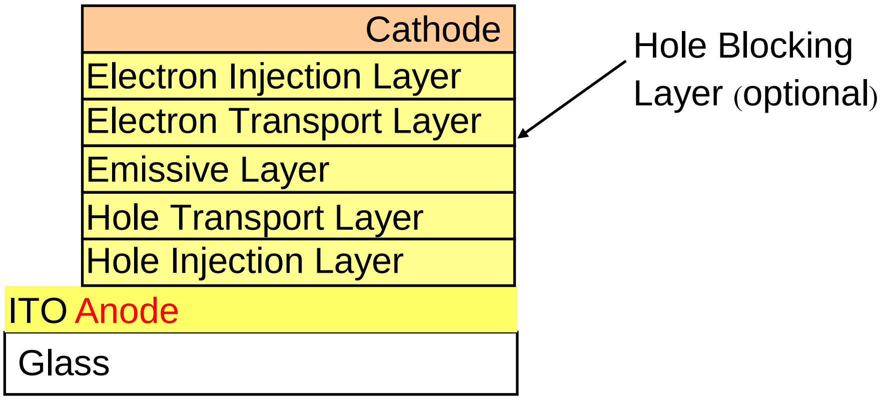


Figure 3: An OLED device with ITO anode

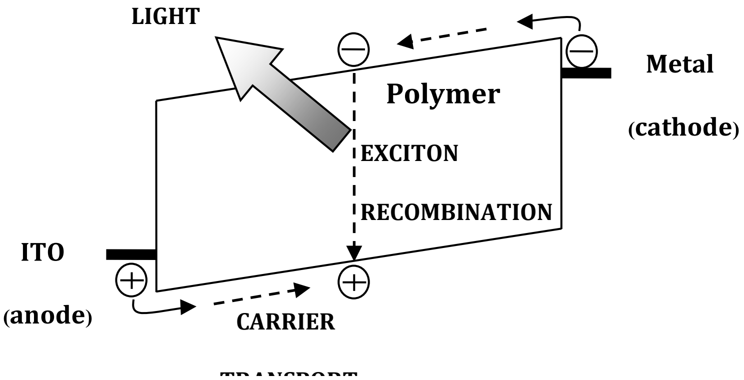


Figure 4: Band diagram of a single layer OLED.

Requirements for the Experiment:

Materials:

1) ITO coated Glass as anode
2) PEDOT:PSS*(poly(3,4-ethylenedioxythiophene) polystyrene sulfonate)* as Hole Injection layer
3) MEHPPV*(Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene])* as emissive layer
4) Ga-In eutectic as cathode
5) DI water, chloroform, toluene, acetone, methanol.

Equipment:

1) Sample holder
2) Multimeter
3) Diamond Cutter Pencil
4) Ultrasonicator
5) Nitrogen Gun
6) Spin coater
7) Hot plate or oven

8) Voltage source
9) Photo diode and current measurement unit.

Other Requirements:

Beakers, Spatula, Tweezers, Syringe, Filter, Petridish, Apron, Gloves, Mask, Head cover, Eye glasses, Cotton swabs, Soap Solution, Tooth Brush, Aluminium Foil

Brief Description of the Experimental procedure

Basic Fabrication Steps:

1. Cleaning of substrates
2. Coating and annealing of HIL and Emissive Layer
3. Deposition of cathode

1. Cleaning the substrates:

1. Wear safety equipments (apron, gloves, mask, head cover, eye glasses).
2. Wash the equipments beakers, syringes, petridish, stand, tweezers and measuring cylinders with DI water and soap. Put them in oven at 110^{0}C. [CHECK: This step may already have been performed before you come to the laboratory]
3. Turn ON the clean bench, if it is not already turned ON. Switch on the air blower from the switch located in front panel of the clean bench.
4. Check which side of substrate is conductive. Conductive side is ITO (anode). Then mark the glass side with some number or alphabet so that one can easily recognize the ITO side.
5. Wash ITO substrates in soap water with the help of a tooth brush (see figure below) and rinse them first in tap water and then in DI water.

Figure 5: Washing Substrate with soap and DI water

6. Place all clean substrates in Teflon sample holder as shown in figure

Figure 6: Placing of substrates in Teflon sample holder

7. Now we clean these substrates by ultrasonication bath. Take 300 ml of DI water in a beaker and place this sample holder in that beaker. Make sure that substrates should be completely dipped in DI water. Put that beaker in ultrasonicator which should be on the clean bench. [ATTENTION: water should be filled 2/3 of the height of ultrasonicator]. Switch on the ultrasonicator by on/off button and set timer for ultrasonication. We can increase/decrease the time in the step of 5 minutes by pressing arrow up/ down button (see figure below). Here we do ultrasonication for 10 minutes.

Figure 7: Substrates placed in ultrasonicator and magnified view of front panel from where we can set time and temperature for ultrasonication

9. Repeat same process for methanol/acetone and DI water for 10 minutes each.

10. Rinse the substrate thoroughly with DI water from the wash bottle; force the water jet on substrate while holding it with tweezers in a slanting orientation. Then dry the substrate with a nitrogen gun and lay the substrates in petridish until all of them are rinsed and dried. Close this petridish with another petridish. Put these substrates in Oven for 10 minutes at 110^0C. After 10 minutes, put the substrates out of the oven and allow them to cool. [NOTE: The substrate with the ITO coated side should always be upside faced]

2. Coating and annealing of HIL and Emissive Layer

2(a). HIL Coating and Annealing

- **Preparation of PEDOT: PSS solution:**

We place PEDOT: PSS (blue color liquid) bottle in refrigerator. Make sure that it will be kept outside 30 minutes prior to use, so that solution of PEDOT: PSS cool down to Room Temperature.

2(b). Spin coating:

Organic layers were deposited over ITO by using the spin-coating technique. In this technique we pour an amount of the organic solutions on the substrates, which are then rotated at high speed in order to spread the liquid by centrifugal force. This procedure quickly evaporates the solvent and creates a uniform solid film whose thickness will depend on the rotational speed, solution viscosity and time of rotation.

1. On switching on the spin coating unit, a message will display as shown in the figure below. First press “1”to warm up the machine. Warm up process will end automatically in 10 minutes. Then press “2” to load program. A message will display “enter program <1/2>”. Then again Press “1”. Now you can set speed, acceleration and time for spin coating. For this press Edit/Save button. A message will display “Prog-1 set number of steps 1/10”. Than press Edit/Save button once more. Use backspace button, left key and right key to alter the RPM or Time for spin coating. Use the same button to save. Now place your substrate on the stage (chuck) made for rotation. A vacuum pump is connected to the unit. Switch on the pump and press the vacuum button located in spinner. It will suck the sample so that the substrate will not fall down during rotation. Then press “Run” button. A **message** will display “press [Run] to start.” Pour the filtered PEDOT: PSS on the substrate by the help of a syringe then press “Run” button again. Stage of spinner will start rotating and after set time it will stop. MAKE sure the lid of spin coater should be closed. Spin coating of PEDOT: PSS is done now. Press “vacuum” button to release the vacuum so that we can remove our sample from the stage. For this lab we will do spin coating of PEDOT: PSS at 1200 RPM for 1 minute.
2. Anneal (put on hot plate/place inside oven) the spin coated substrates at a temperature of 140^{o}C for 10 minutes.
3. Cool the substrates to room temperature for 5 minutes by placing sample down from the hot plate before coating the emissive layer.

Figure 8: spin coating unit

2 b). Emissive Layer:

1. Take solution of MEHPPV (made in toluene with concentration of 8 mg/ml) and filter it with a 0.1micron filter before coating.
   [NOTE: Solution must be magnetically stirred at least for 6-8 hours]
2. Spin coat it at 1200 rpm for 1 minute. Spin coating procedure will be same as above. Figure shown below demonstrates spin coating of MEHPPV.
3. Anneal it at 140°C for about 10 minutes and cool down to room temperature.

Figure 9: MEHPPV coating using spin coater

3. Cathode deposition

In standard technique Al/Ca is deposited via thermal vapor deposition technique.

Here GaIn is used. Use mask with circular aperture in which GaIn should be applied with a cotton swab as shown in figure below. (Note that Ga-In is in liquid form at room temperature). Alternatively, GaIn cathode contact dots can also be coated without using a mask, with the help of cotton swabs

Figure 10: Application of Ga-In contact dots with cotton swab as cathode

4. Characterization

1. Apply appropriate voltage to check functionality of device and note down the colour of light generated from it.
2. Measure I-V characteristics of fabricated device and calculate the threshold/turn-on voltage and rectification factor from the current-voltage plot.
3. Also observe and record the electroluminescence (EL) of the fabricated device and calculate the band gap (E_g) from the EL spectrum.

5. Precautions

1. Always wear the safety equipment prior to performing the experiment.
2. Substrate should always be help with the help of tweezers and should be placed on the petridish with its ITO coated side facing upside to avoid contamination.
3. Connections while measuring the I-V characteristics and light output should be made carefully in order to prevent the device from getting punctured.

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EXPERIMENT-5

Understanding Magnetic Behaviour of Materials

Aim:

Understanding the magnetic behavior of materials by measuring the hysteresis curve and calculation of magnetic properties namely, remnant magnetization, coercive field and magnetic moment per atom.

Background:

Magnetic Materials

There are four basic type of magnetism that occur in a variety of materials. The most fundamental of all is diamagnetism which is an intrinsic characteristics of all atoms whilst other forms are magnetism such as paramagnetism, ferromagnetism and ferrimagnetism are specific characteristics of certain materials.

Diamagnetism

Diamagnetism is a very weak form of magnetism that is nonpermanent and persists only while an external field is being applied. It is induced by a change in the orbital motion of electrons due to an applied magnetic field. The magnitude of the induced magnetic moment is extremely small, and in a direction opposite to that of the applied field, as shown Figure 6.1. Thus, the relative permeability is less than unity (however, only very slightly), and the magnetic susceptibility is negative; that is, the magnitude of the B field within a diamagnetic solid is less than that in a vacuum. Diamagnetic susceptibility, χ_m, is given as

$$\chi_m = \frac{M}{H} = -\frac{N e^2 \bar{r}^2 \mu_o}{6m}$$

where M is magnetization (magnetic moment per unit volume), H is the applied magnetic field, N is the number of electrons per unit volume, e is electron charge ($1.6\text{x}10^{-19}$ C), r is the orbital radius, μ_o is the permeability of free space and m is the mass of electron ($9.1\text{x}10^{-31}$ Kg).

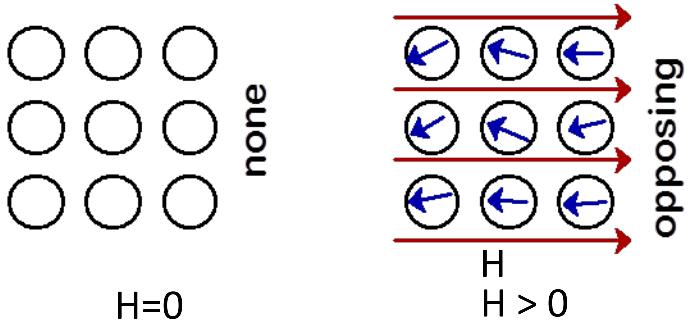


Fig-6.1: The atomic dipole configuration for a diamagnetic material with and without a magnetic field. In the absence of an external field, no dipoles exist; in the presence of a field, dipoles are induced that are aligned opposite to the field direction.

Paramagnetism

For some solid materials, each atom possesses a permanent dipole moment by virtue of incomplete cancellation of electron spin and/or orbital magnetic moments. In the absence of an external magnetic field, the orientations of these atomic magnetic moments are random, such that a piece of material possesses no net macroscopic magnetization. These atomic dipoles are free to rotate, and paramagnetism results when they preferentially align, by rotation, with an external field as shown in Figure 6.2. These magnetic dipoles are acted on individually with no mutual interaction between adjacent dipoles. Inasmuch as the dipoles align with the external field, they enhance it, giving rise to a relative permeability that is greater than unity, and to a relatively small but positive magnetic susceptibility. Susceptibilities for paramagnetic materials range from about to 10^{-5} to 10^{-2}. Paramagnetic susceptibility is given by

$$\chi = \frac{M}{H} = \frac{N\mu_m{}^2\mu_o}{3kT}$$

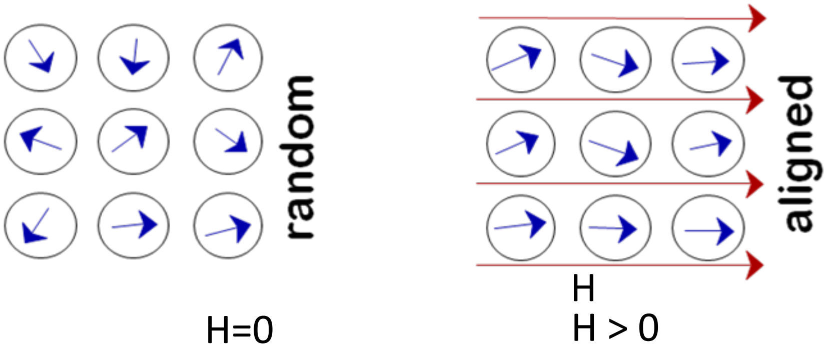


Fig-6.2: Atomic dipole configuration with and without an external magnetic field for a paramagnetic material.

A schematic B-versus-H curve for a paramagnetic material is also shown in below in Fig. 6.3. Both diamagnetic and paramagnetic materials are considered to be nonmagnetic because they exhibit magnetization only when in the presence of an external field. Also, for both, the flux density B within them is almost the same as it would be in a vacuum

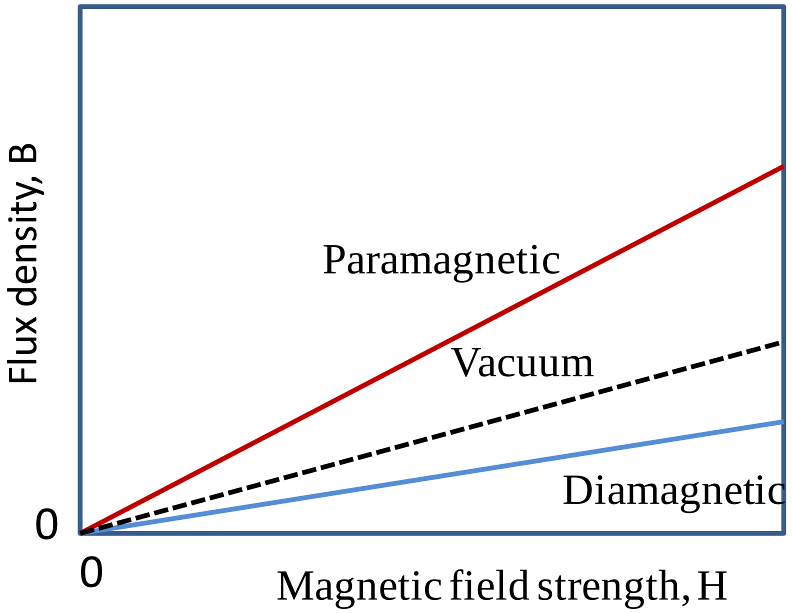


Fig-6.3: Schematic representation of the flux density B versus the magnetic field strength H for diamagnetic and paramagnetic materials ($B=\mu_o H$)

Table 6.1 Room-Temperature Magnetic Susceptibilities for Diamagnetic and Paramagnetic Materials

Diamagnetics		***Paramagnetics***	
Material	***Susceptibility X_m (volume) (SI units)***	***Material***	***Susceptibility X_m (volume) (SI units)***
Aluminum oxide	-1.81×10^{-5}	Aluminum	2.07×10^{-5}
Copper	-0.96×10^{-5}	Chromium	3.13×10^{-4}
Gold	-3.44×10^{-5}	Chromium chloride	1.51×10^{-3}
Mercury	-2.85×10^{-5}	Manganese sulfate	3.70×10^{-3}
Silicon	-0.41×10^{-5}	Molybdenum	1.19×10^{-4}
Silver	-2.38×10^{-5}	Sodium	8.48×10^{-6}
Sodium Chloride	-1.41×10^{-5}	Titanium	1.81×10^{-4}
Zinc	-1.56×10^{-5}	Zirconium	1.09×10^{-4}

Ferromagnetic Materials

All ferromagnetic magnetic materials exhibit spontaneous magnetic moment - a magnetic moment even in zero magnetic field. They have ordered arrays of magnetic moments, *i.e.* electron spins and spin magnetic moments are arranged in a regular manner, as illustrated in Fig. 6.4. Magnetic materials can be classified into ferromagnetic [spins aligned in the same direction or parallel, equal moments of one type only, e.g. Fe, Co, Ni, Gd], antiferromagnetic [spins on neighboring atoms in opposite directions or antiparallel, all moments of one type only and equal, net saturation magnetic moment nil, e.g. Cr], and ferrimagnetic [spins on neighboring atoms in opposite directions or antiparallel, but more than one type of moment present with unequal moments, for example in ferrites such as $NiFe_2O_4$ or $NiO.Fe_2O_3$].

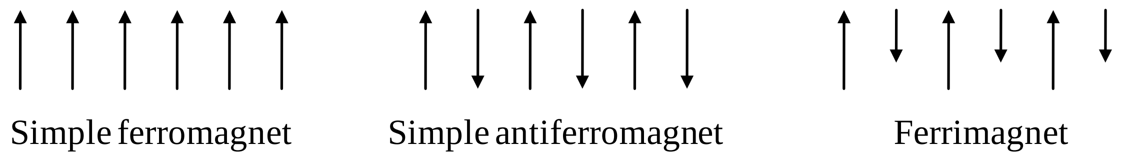
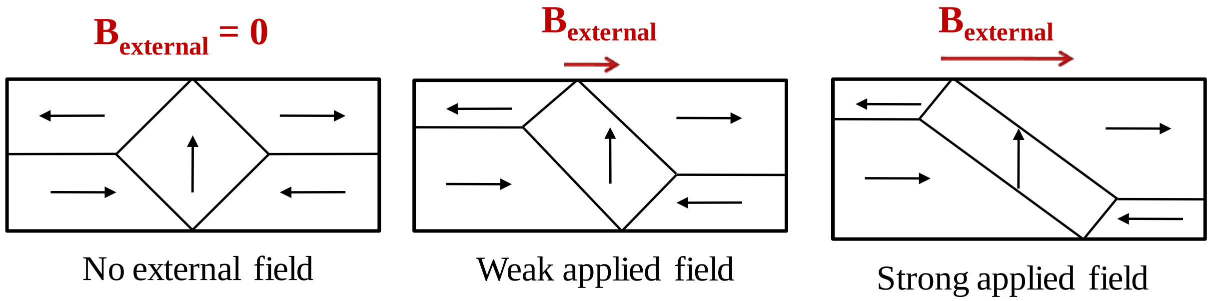

Simple ferromagnet Simple antiferromagnet Ferrimagnet

Fig-6.4: Possible ordered arrangements of electron spins.

Ferromagnetic Domains

In a ferromagnetic specimen, often, the net magnetic moment is much less than what one would expect from the sum of magnetic moments of all the individual atoms, and application of an external magnetic field is required to obtain the saturation magnetic moment. This phenomenon is explained by the presence of magnetic domains. A domain is a small region in a magnetic material, within which the local magnetization is saturated, i.e. spins on all the atoms are parallel. However, the directions of magnetization of different domains do not coincide, as illustrated in Fig. 6.5, resulting in a small resultant magnetic moment.



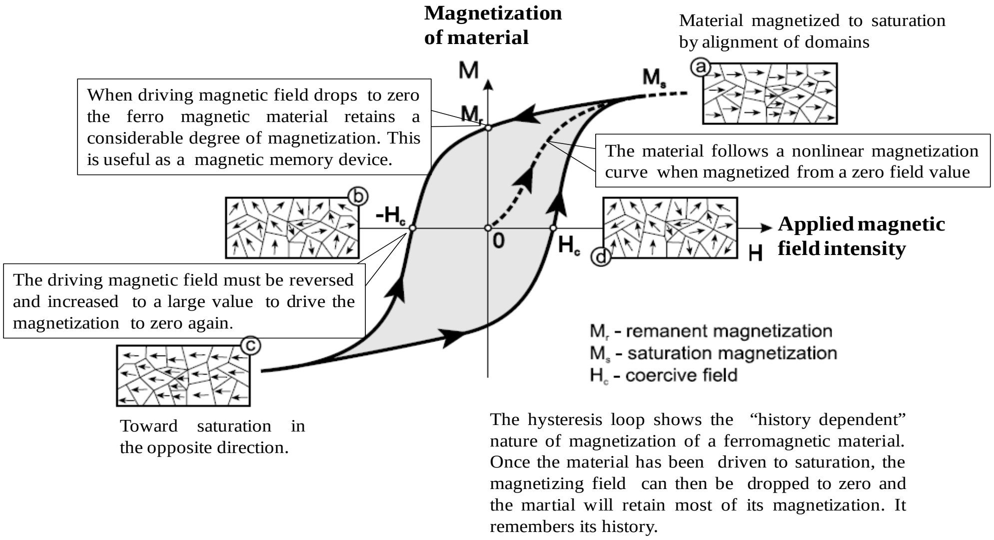
No external field Weak applied field Strong applied field

Fig-6.5: Magnetic domains behavior with applied field

Magnetic domains are responsible for the hysteresis loop. Fig.6.5 represents the magnetization curve, i.e. magnetization M as a function of the external magnetic field H, of a ferromagnetic materia1. It is assumed that the net magnetization was zero for the specimen, before the application of the external magnetic field. The increase in the magnet moment of the specimen under the action of an applied magnetic field takes place by two independent processes:

[i] in weak applied fields, the volume of domains which are favorably oriented with respect to the field increases at the expense of unfavorably oriented domains, See Fig. 6.5

[ii] in strong applied fields, the magnetization rotates toward the direction of the field.



Material magnetized to saturation by alignment of domains

When driving magnetic field drops to zero the ferro magnetic material retains a considerable degree of magnetization. This is useful as a magnetic memory device.

The material follows a nonlinear magnetization curve when magnetized from a zero field value

The driving magnetic field must be reversed and increased to a large value to drive the magnetization to zero again.

Toward saturation in the opposite direction.

The hysteresis loop shows the "history dependent" nature of magnetization of a ferromagnetic material. Once the material has been driven to saturation, the magnetizing field can then be dropped to zero and the martial will retain most of its magnetization. It remembers its history.

Fig 6.5: Magnetization behaviour of a ferromagnetic sample in the form of magnetization (M) vs applied field (H) loop.

These two processes can explain why a loop is traced in the B-H plane, as the magnetic field completes a cycle. Technical terms defined by the hysteresis loop are shown in Fig.6 5. The domain structure of ferromagnetic materials affects their practical properties. In a transformer core, we want a high permeability = B/H. In a permanent magnet, we want a high coercive force. By suppressing the possibility of boundary displacement, we may achieve a high coercivity, the suppression may be accomplished by using very fine particles or by precipitating a second metallurgical phase, so that the specimen is heterogeneous on a very fine scale. By making the material pure homogeneous and well oriented we facilitate domain boundary displacement, and thereby attain high permeability. The area of the hysteresis loop represents an energy loss. In industrial applications, magnetic materials are classified on the basis of the loop area and characteristics. Soft magnetic materials have low hysteresis and eddy current losses, and high magnetic permeability. [Eddy currents flow in a magnetic material due to the induced EMF. This current has a corresponding I^2R loss.] These materials [e.g. 97Fe3Si, FeO, NiO.FeO] industrially are most important. Hard magnetic materials [e.g. ALNICO5: 51Fe14Ni24Co8A13Cu], on the other hand, have high coercivity, and large remanent and saturation magnetizations. Hence, to characterize any magnetic material, it is necessary to obtain its hysteresis loop.

Magnetic moment calculations

Magnetic dipole moment = Saturation Magnetization * Volume of the sample
Saturation Magnetization is in A/m
Magnetic dipole moment of the entire sample in $A.m^2$
Step1: Find number of atoms in the sample volume
Step2: Dividing overall dipole moment with number of atoms gives dipole moment per atom
Step3: Convert $A.m^2$ into Bohr magneton.

The experiment:

Measurement Setup:

The hysteresis loop measurement setup has three components:
[i] the solenoid specimen- pickup coil combination;
[ii] the loop tracer control cabinet; and
[iii] the oscilloscope for loop tracing.

The magnetic specimen is a Ni wire, 1.13 mm in diameter, 44 mm in length. To obtain its hysteresis loop, the ac hysteresis loop tracer will be used. The magnetic field is provided by a solenoid, into which the magnetic specimen is placed. A pick-up coil is used to monitor the magnetization of the specimen. The specimen, the pick-up coil, and the solenoid are, coaxial. The pick-up coil is shorter than the specimen in length, is located in the center of the specimen, and closely encircles the specimen. The hysteresis loop tracer feeds to the x-axis of an oscilloscope a signal proportional to the magnetic field H, and to the y-axis a signal proportional to the magnetization M. Hence, as the applied magnetic field is sinusoidal, a loop is traced on the oscilloscope, for a given magnitude of the applied sinusoidal magnetic field. This loop will not only increase in size with the magnitude of the sinusoidal field, but will also change in shape. For low to medium magnitudes, the loop shape will be rectangular to parallelogram. At high magnitudes, it will approach the form of Fig. 6.3, and will indicate saturation of magnetization. Several problems are encountered in practice while measuring the hysteresis loop. The magnetic field becomes non-uniform on account of: [i] open specimen; and [ii] fields induced by the eddy current. The eddy currents also cause the forward and backward paths traced near saturation magnetization to be different, thereby leading to a small loop inside the large loop in the saturation region.

Brief Description of the Experimental procedure

1. Inspect the measurement setup, in particular the solenoid-specimen-pickup-coil combination and the loop tracer control panel.

2. Calibration of the oscilloscope and settings of the area ratio and demagnetization factor.

(a) Settings: Without sample. Oscilloscope at D.C. Time base EXT., H Bal., Phase and DC Bal. adjusted for horizontal straight line in the centre. Demagnetization at zero and area ratio 0.4 at magnetic field 200 guass

(b) Adjustment: By adjusting N and (As/Ac) as given above the J-H loop width is too small. Thus both are adjusted to three times i.e. 0.405 and 0.0099 (full value of area ratio pot.=1.000, full value of dmag. Pot.=0.100) respectively.

3. Record:
[i] loop shape;
[ii] loop width [in mm];
1V(Big Division) =10mm (Volts to mm conversion)
On X-axis one small division = 2mm (X-axis should be measured in mm)
On Y-axis one small division = 0.2V
[iii] tip to tip height [in mV]; and
[iv] y-axis intercept, [in mV] for magnetic fields of 50, 100, 150, 200, 250, and 300 Gauss.

4. The loop shape is to be recorded as free-hand sketches on the result sheet. The values of field, loop width, tip to tip height, and y-axis intercept are to be put in a tabular form.

5. From the table, estimate the saturation magnetization M_s in mV [= half the asymptotic value of the tip to tip height], the remanent magnetization M_r in mV [= r the asymptotic value of the y-axis intercept]. To estimate the coercivity H_C in mm, plot on a small-size graph paper the loop width versus the field. Take H_c as half the value of the intercept of the linear part of the plot for zero field.

6. Calculate H_c in Oersted, M_r in Gauss, M_s in Gauss, and from guass convert M_r, M_s to A/m using the following relations:

1 mm = 8.58 O_e 1mV= 2.63 G   1 G = 80 A/m

Expectations from the Students:

- **i.** Prior reading & understanding of Basics of magnetism, terminology, units etc..
- **ii.** First measure the loops for Fe and Ni wires using the above procedure. Using appropriate conversion factors, calculate the **magnetic moment in Bohr magneton** (μ_B) per atom for both Fe and Ni samples. Do these two values differ? If yes, why and if not, why not? Compare these moments with those theoretically achievable and discuss any discrepancy.
- **iii.** You are also provided pieces of copper, tungsten and chromium wires. Measure their hysteresis loop. Just what you see and also understand what is expected? Any difference between the expected and observed behaviour should be understood.
- i. Correlate all your observations, measured properties with magnetic moments, Domain alignment, electronic configurations, susceptibility, permeability etc..

References:

1. A.J. Dekker, Solid State Physics, Macmillan & Company
2. Rolf E. Hummel, Electronic Properties of Materials, Springer

EXPERIMENT - 6

SEMICONDUCTOR CHARACTERIZATION

(1) Aim

Characterize semiconductor material to find out its band-gap and dopant-concentration in it.

(2) Introduction

Information about many characteristics of a system can be obtained by disturbing it away from its equilibrium state with the help of external stimuli. This is what we will be doing for the two semiconductor devices, both diodes, in order to know about the important characteristics mentioned below for semiconductors involved in these devices.

(1) Band-gap, and
(2) Dopant concentration as a function of depth

Band-gap

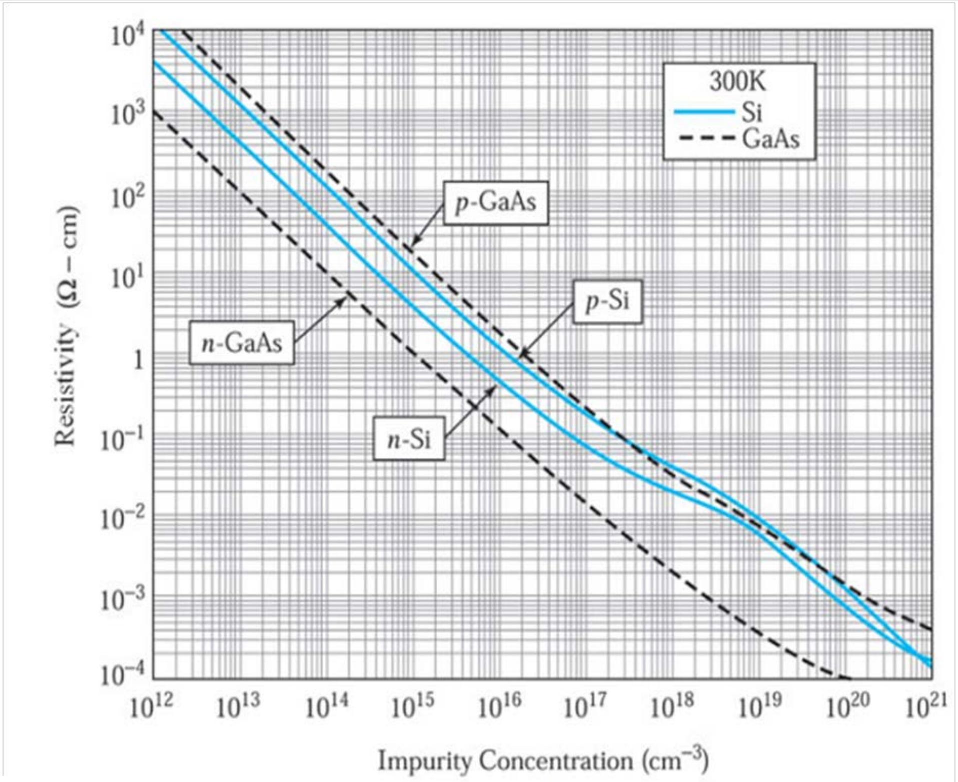
This is the minimum energy that an electron from the energy-level at the upper-edge of valance-band requires in order to jump to the energy-level at the bottom-edge of conduction band. Knowing Band-gap of a material helps us predict whether a material will be insulator or semiconductor at the temperature of interest. It can also give us an idea about the frequency and thus the colour of light emitted from light-emitting diodes made of a given semiconductor. In a solar-cell what part of the incident radiation would be absorbed and hence could (depends on many other factors) be converted into electricity, is determined by the bad-gap of the semiconductor used in that solar-cell. Pure glasses are transparent because their band-gap is large and thus the photons from the visible part of the solar-spectrum are not absorbed. From these examples it is evident that finding out band-gap of a semiconductor or insulator is important.

(Note that for metals we do not talk about band-gap because for them the highest occupied energy-band is partially filled. In some cases one would predict an element to have the highest occupied energy-band to be fully filled, however, due to energy-overlap between this fully filled energy band and the next higher energy empty band, some electrons spill into this otherwise empty band. This results into a partially filled highest occupied energy-band and hence metallic behaviour.)

In the ***part A*** of present experiment we will measure forward-bias across the two terminals of a diode as a function of its temperature, and use this information to extract the value of band-gap of semiconductor that has been used for this diode.

Dopant concentration

The semiconductors have found so much importance as electronic materials because of our ability to control the magnitude and type (n or p-type) of conductivity in these materials by controlling the concentration and type of impurities, respectively. These impurities are called dopants; in general, useful impurities are called *dopants*, while, undesired impurities are called *impurity*. One can get a feel of effect of impurities on the conductivity of semiconductor by observing the plot for resistivity (= 1/conductivity) vs. dopant concentration shown in *figure 1*. It gives us an idea about the order of magnitude of change in the resistivity of a semiconductor due to change in the concentration of dopants. Therefore, depending on the application, introduction of controlled amount and distribution of impurities in a semiconductor is very important. In the **part B** of this experiment we will use capacitance-voltage measurements on a Schottky-barrier diode to extract information about dopant-concentration as a function of depth from the surface (actually metal-semiconductor interface in this case) of semiconductor used in this Schottky-barrier diode.



Resistivity versus impurity concentration^3 for Si and GaAs.

Figure 1

Part (A)

(1)Objective:

Determine band-gap of a semiconductor used in a given homojunction p-n diode.

(2)Technique/Approach:

Analyze the change in forward-bias as a function of temperature for the given p-n diode.

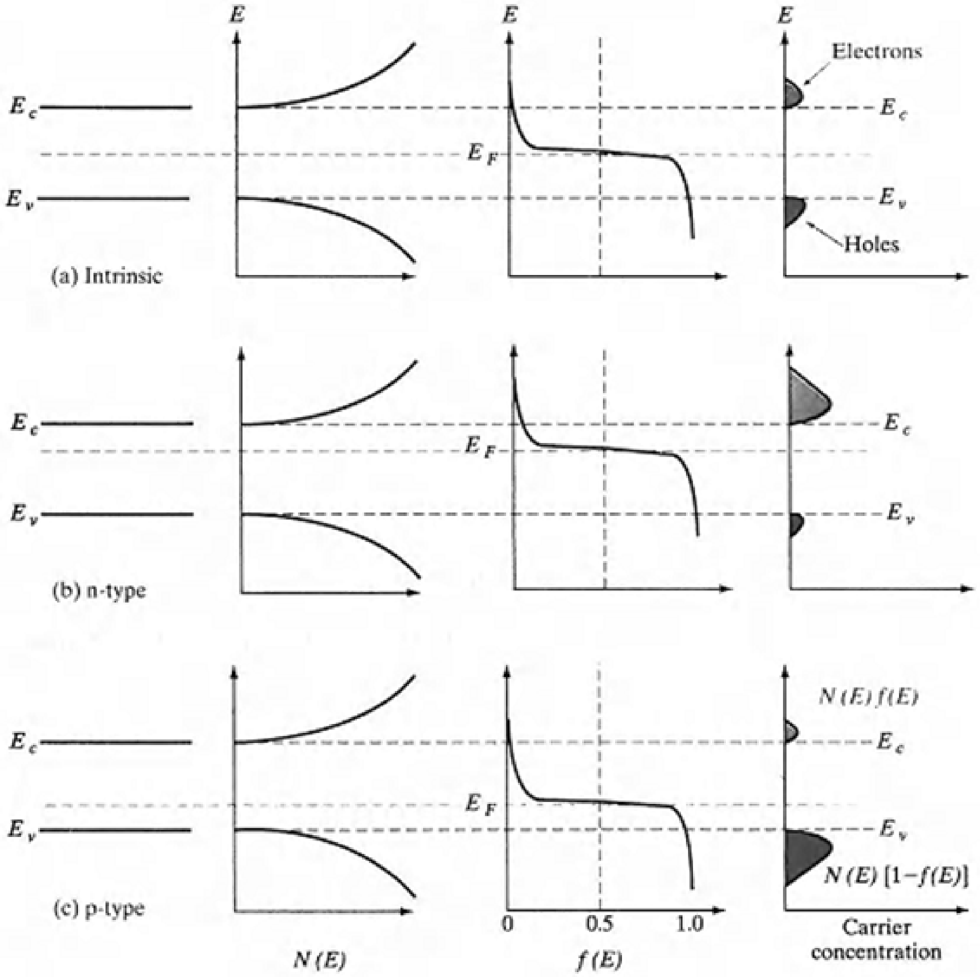
(3)Theoretical background:

In order to design an experiment for this purpose you will need to understand following characteristics of a diode, and the closely related characteristics of the semiconductor involved in that diode.

(a) Fermi energy-level

Relative position of Fermi-energy level in a semiconductor indicates the chemical potential of electrons in that material compared to another material. We can roughly visualize this level as being indicative of electron-pressure inside that semiconductor. Using this approximation, similar to what would happen upon connecting two gas containers with different gas-pressure, one can visualize the natural tendency of diffusive-flow of electrons from one material to another upon electrically connecting them. To be specific, the natural tendency of electrons to diffuse will be from higher Fermi-energy material to the lower Fermi-energy material when a junction is formed between them while both of them are at same temperature. Mathematically, if we look at the Fermi-Dirac distribution function which is a statistical-distribution function for electrons and other similar quantum-mechanical particles collectively called Fermions, one can see that the Fermi-energy is that energy at which the probability of finding an electron is 1/2.

In an n-type semiconductor since there are more electrons in conduction band compared to holes in the valence-band, the Fermi energy-level is closer to conduction energy-band edge compared to that in an intrinsic semiconductor. It is exactly opposite in a p-type semiconductor where the Fermi energy-level is closer to the valence energy-band edge. See *figure 2* below.

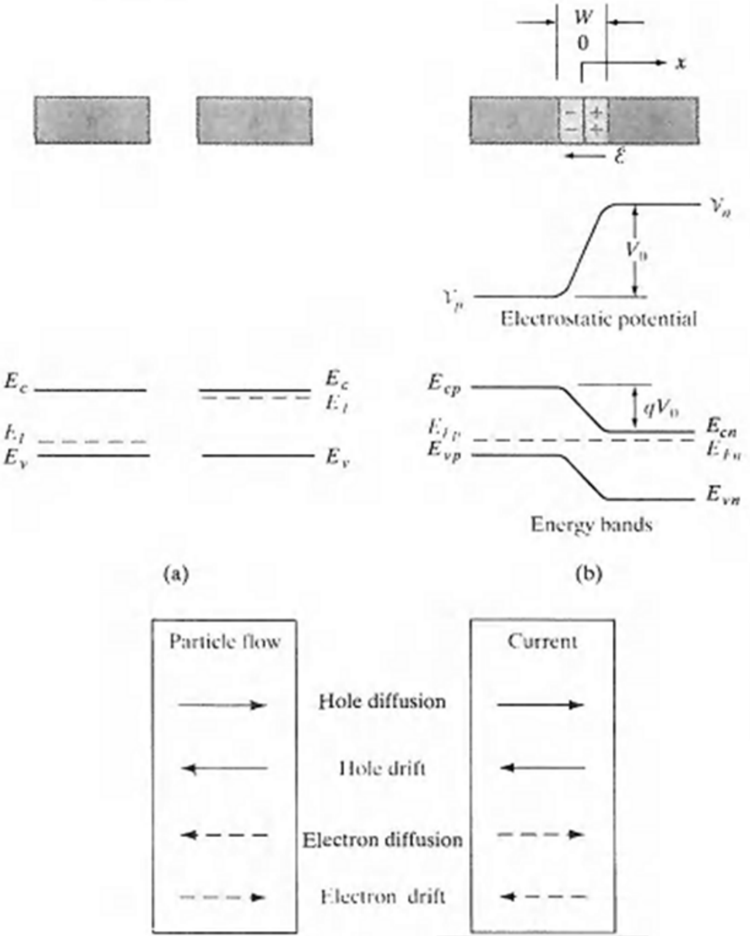


Schematic band diagram, density of states, Fermi–Dirac distribution, and the carrier concentrations for (a) intrinsic, (b) n-type, and (c) p-type semiconductors at thermal equilibrium.

Figure 2

(b)p-n Diode and built-in voltage

A diode can be thought of being made by bringing a p-type and an n-type semiconductor together to form a physical as well as electrical contact/junction between them. The moment this contact is established, due to mismatch of Fermi-levels in the two the electrons diffuse from semiconductor having higher Fermi-energy level (n-type in this case) to the semiconductor having lower Fermi-energy level (p-type in this case). As the electrons from n-type material enter in the p-type material they combine with the majority charge-carriers of p-type, that is, holes, and as a result negatively charged acceptor ions in the p-type and positively charged ions in the n-type semiconductor are left behind near the junction. This build-up of immobile charges leads to an electric field directed from the n-type semiconductor (positively charged immobile ions near the junction) to p-type semiconductor (negatively charged immobile ions near the junction). This electric-field exerts electrostatic attraction on the diffusing electrons; this force is directed from p-type semiconductor to n-type semiconductor, and it is exactly opposite to the direction of diffusion of electrons which is from n-type semiconductor to p-type semiconductor. In the beginning the electric field doesn't exist, however, as the diffusion continues across the junction and immobile charges build-up on two sides of it, an electric-field and a corresponding potential difference gradually builds-up. When the opposite forces experienced by the electrons, one due to the electric-potential difference and another due to the chemical-potential difference become equal in magnitude the flow of charge-carriers across the junction stops. The potential-difference that builds-up at equilibrium state is known as built-in potential (V_{bi}). The region near the junction where there are no holes or electrons (that is, mobile charges) is called depletion-region or space-charge region. From the *figure 3* below it can be seen that the magnitude of built-in potential is equal to the potential difference between the two Fermi energy-levels (n and p-type) of the semiconductors forming a junction (hold on to this observation, we will come back to it).



Properties of an equilibrium p-n junction: (a) isolated, neutral regions of p-type and n-type material and energy bands for the isolated regions; (b) junction, showing space charge in the transition region W, the resulting electric field ℰ and contact potential V_0, and the separation of the energy bands; (c) directions of the four components of particle flow within the transition region, and the resulting current directions.

Figure; 3

(c) Forward-bias and forward-current

In the forward-bias condition n-type side of the diode is connected to the negative polarity of external power supply and p-type is connected to positive polarity. For forward biased diode the electron flow from n-type to p-type semiconductor, and from the *figure 3* you can see that before the flow can establish the electrons would have to cross the built-in potential barrier. This is the reason why a finite (non-zero) forward-bias called *Threshold-voltage* (see *figure 4*) has to be applied before getting any forward-bias current. Larger the built-in potential larger is the *Threshold-voltage*, and hence larger forwards-bias has to be applied for getting a given amount of current to flow.

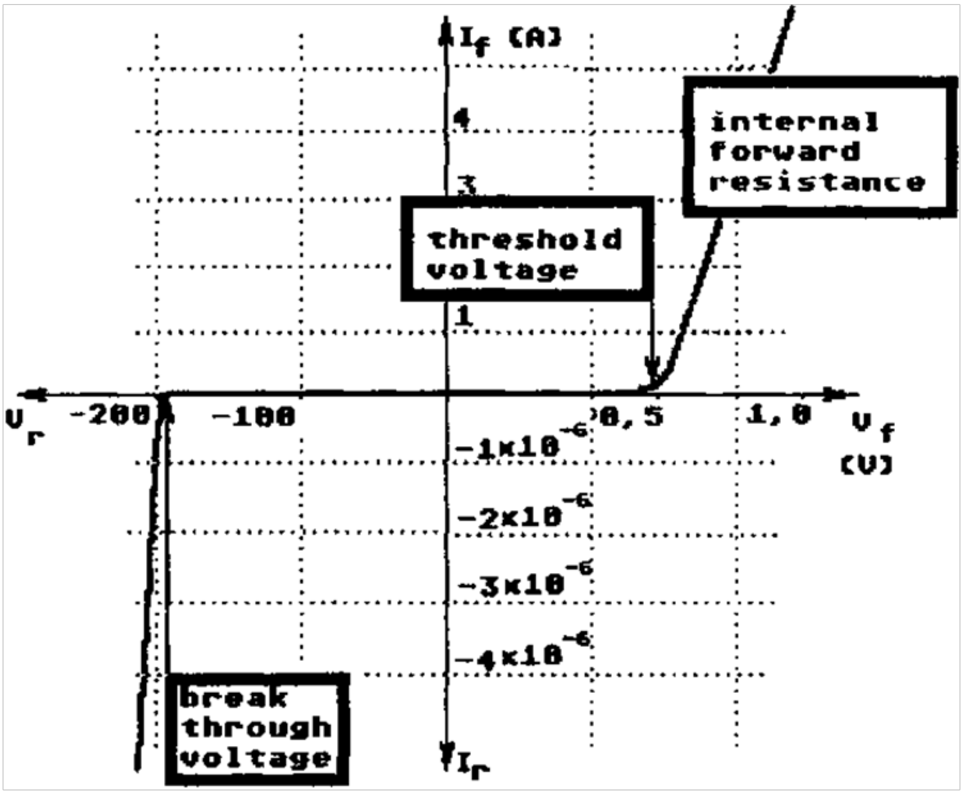
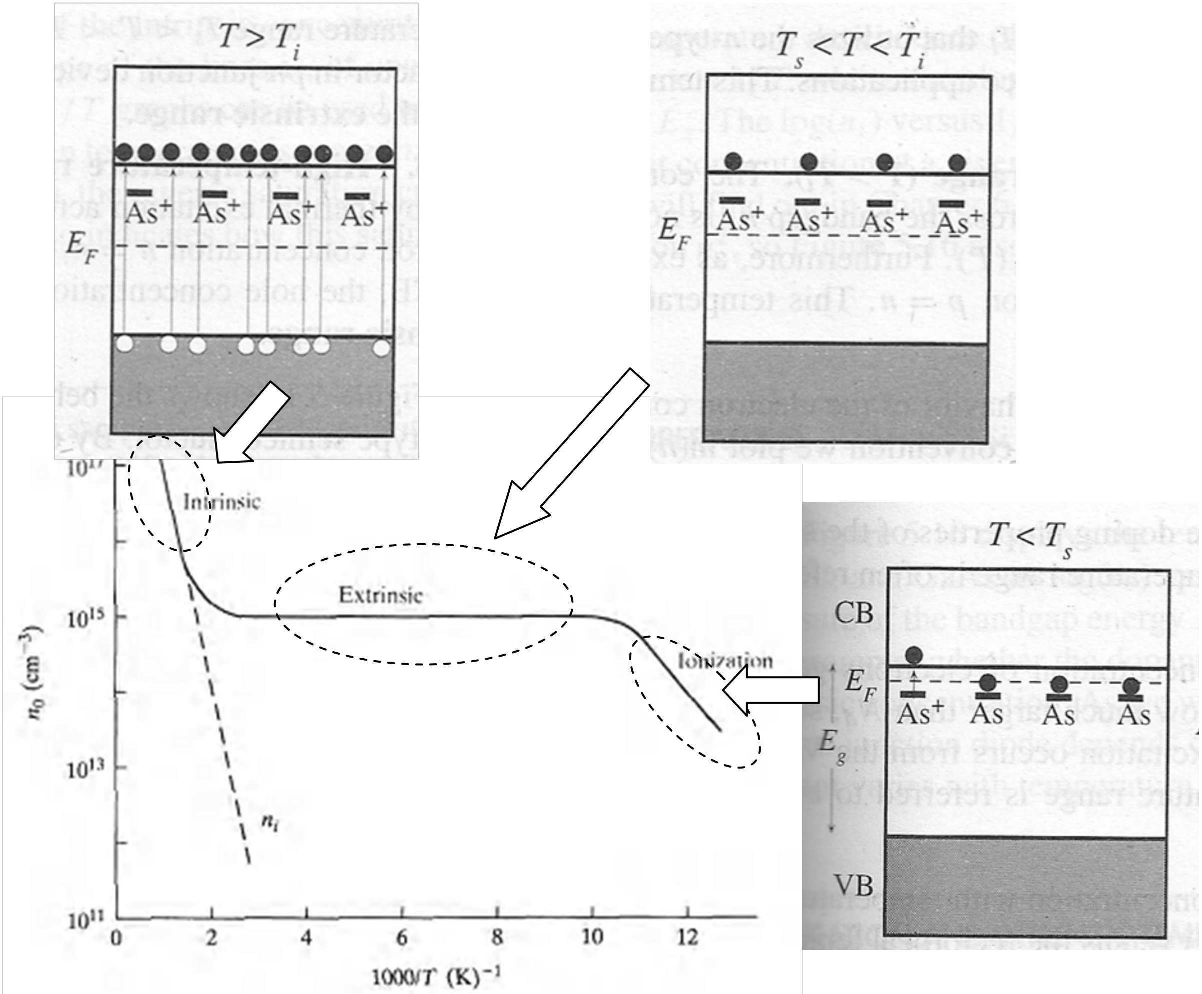


Figure 4

(d) Changes that happen in the charge carrier concentration in a semiconductors upon heating it

You have seen in one of the ESO214/205 laboratory experiments last year that as we gradually increase temperature of a semiconductor, after certain particular temperature above the room temperature its conductivity starts increasing. This is due to increased thermal energy (~kT) of valence-band electrons enabling them to excite across the band-gap to the conduction band. Upon continuing the increase in temperature, ultimately the concentration of electrons and hole will become equal and thus the Fermi-energy-level will also gradually move from its room temperature location to the centre of the band-gap region. Notice the position of Fermi-energy-levels in the schematics of *figure 5*.



(a) Below T_s, the electron concentration is controlled by the ionization of the donors.
(b) Between T_s and T_i, the electron concentration is equal to the concentration of donors since they would all have ionized.
(c) At high temperatures, thermally generated electrons from the VB exceed the number of electrons from ionized donors and the semiconductor behaves as if intrinsic.

Figure 5

Therefore in brief, we observe the following interdependencies (temperature is constant):

(🡐 ≡ "in governed by" in the following)

1. Magnitude of forwards-bias in order to obtain a particular forward-current 🡐 Built-in potential
2. Built-in potential 🡐 Difference in the Fermi energy-levels in the two semiconductors
3. Difference in the Fermi energy-levels in the two semiconductors of fixed dopant concentration 🡐 Temperature of the semiconductors
4. When would a semiconductor start changing from an external type to intrinsic type semiconductor upon increase in its temperature is governed by its band-gap energy.

Now let us connect these individual interdependencies and use them to analyse a situation where a diode is being heated. During this heating, from section (d) above, it can be said that the energy-difference between the Fermi energy-levels of two semiconductors forming the junction will decrease; this in turn, based on the discussion in section (b) and (c), will lead to reduction in built-in potential and hence the reduction in the threshold-voltage. Therefore, as a diode is gradually heated, it would be expected to require less and less forward-bias in order to maintain same forward-current. See the current – voltage plot of a diode at different temperatures in *figure 6*.

From this discussion we see that by studying the change of forwards-bias of a diode as a function of temperature while holding the forward-current to a constant, one can extract information about the band-gap of semiconductor.

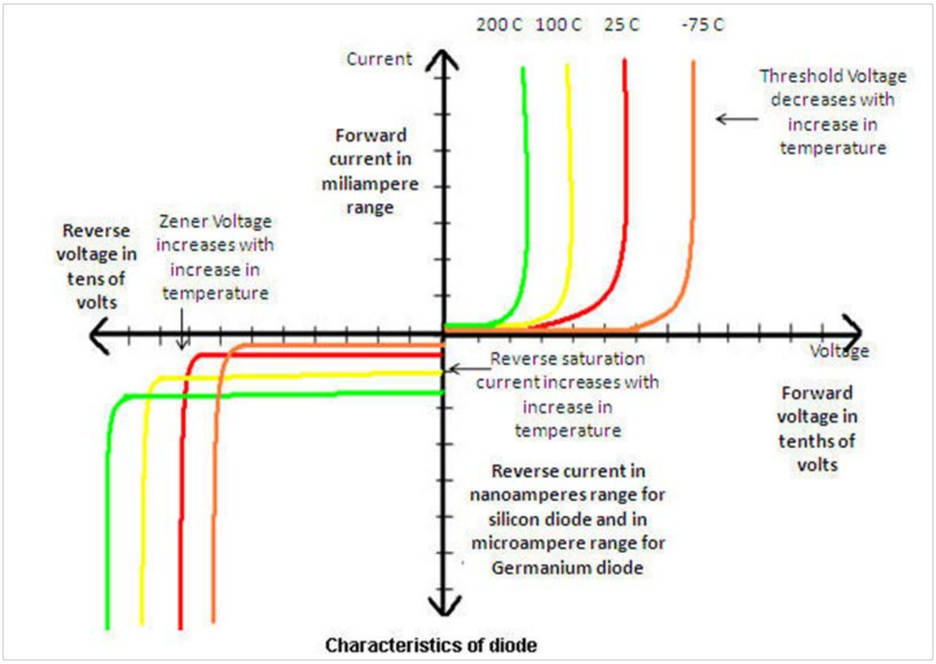


Figure: 6

(4)Designing the experiment which utilizes the observations in section (3) above.

We need to put what we discussed in section (3), into a mathematical form. Since we want to hold forward-bias current constant while measuring the corresponding forward-bias as a function of diode temperature, we should start with an expression which could connect all of these parameters; the following well established expression for diode-current can do this job for us.

$$\boxed{I = qA\left(\frac{D_p}{L_p}p_n + \frac{D_n}{L_n}n_p\right)(e^{qV/kT} - 1) = I_0(e^{qV/kT} - 1)}$$

I : Diode-current

I_0 : Reverse-bias current

D_p : Diffusion-coefficient of holes

D_n : Diffusion-coefficient of electrons

L_p : Diffusion-length of holes ~ $\sqrt{D_p \tau_p}$; τ_p is average life-time of holes before they recombine with electrons.

L_p : Diffusion-length of electrons ~ $\sqrt{D_n \tau_n}$; τ_n is average life-time of electrons before they recombine with holes.

p_n : Hole (minority carriers) concentration in the n-type semiconductor

n_p : electron (minority carriers) concentration in the p-type semiconductor

V : Forward-bias across the diode

A : Cross-sectional area of diode; q : Charge (without sign) of an electron; k : Boltzmann constant; T : temperature of diode

A brief note about the above expression: The pre-exponential term involves diffusivity, life-time (τ) and concentration of minority carriers. This is so because when a diode is forward-biased above the threshold voltage, the holes from p-side where they are majority carriers are injected into n-side where they are minority carriers. Since the expression (I vs. V) above assumes that beyond the depletion-region there is no electric-field, the injected holes into the n-side will not be experiencing any electric-field, and therefore no drift; the only way for their transport beyond the depletion region into the n-side is diffusive-transport, and this is why diffusivity and diffusion-length terms appear in the expression for diode-current. Similar description for the electrons injected into the p-side. Note that in a semiconductor the transport of both the electrons and holes contribute towards the current, although, usually one of them dominates in extrinsic semiconductors.

The diode current expression can be further simplified to be useful for this experiment:

$$I = qA\left(\sqrt{\frac{D_p}{\tau_p}}\frac{n_i^2}{n_n} + \sqrt{\frac{D_n}{\tau_n}}\frac{n_i^2}{p_p}\right)\left(e^{qV/kT} - 1\right)$$

$$I = qA\left(\sqrt{\frac{D_p}{\tau_p}}\frac{1}{n_n} + \sqrt{\frac{D_n}{\tau_n}}\frac{1}{p_p}\right)N_C N_V \ \mathrm{e}^{-\mathrm{E_g}/kT}\left(e^{qV/kT} - 1\right)$$

$$I = qA\left(\sqrt{\frac{D_p}{\tau_p}}\frac{1}{n_n} + \sqrt{\frac{D_n}{\tau_n}}\frac{1}{p_p}\right)\left(4\left[m_n^* m_p^*\right]^{3/2}\left(\frac{k}{2\pi\hbar^2}\right)^3\right)\mathrm{T}^3 \ \mathrm{e}^{-\mathrm{E_g}/kT}\left(e^{qV/kT} - 1\right)$$

n_i : intrinsic charge carrier concentration (depends on temperature)

n_n : concentration of electrons in the n-type semiconductor at thermal equilibrium

p_p : concentration of electrons in the n-type semiconductor at thermal equilibrium

N_C : Effective density of states in the conduction-band

N_V : Effective density of states in the valence-band

E_g : Band-gap of the semiconductor

m_n^* : effective-mass of electron

m_p^* : effective-mass of hole

The last expression for current, above, could be approximated to the following expression by assuming that the concentration of majority charge carriers remains almost same as that of the donar/acceptor concentration in the temperature range we will carry out our experiment.

$$I \cong qA\left(\sqrt{\frac{D_p}{\tau_p}}\frac{1}{N_D} + \sqrt{\frac{D_n}{\tau_n}}\frac{1}{N_A}\right)\left(4\left[m_n^* m_p^*\right]^{3/2}\left(\frac{k}{2\pi\hbar^2}\right)^3\right)\mathrm{T}^3 \ \mathrm{e}^{-\mathrm{E_g}/kT}\left(e^{qV/kT} - 1\right)$$

The ratio of diffusivity (D) and life-time (τ) is proportional to T^{γ} where $\boldsymbol{\gamma}$ is some constant. Therefore the above expression can be written as,

$I \approx qAT^{3+(\gamma/2)}\, e^{-E_g/kT}\left(e^{qV/kT} - 1\right)$

We can neglect the $T^{3+(\gamma/2)}$ term in comparison to other temperature-dependent terms which are exponentially dependence on T, and hence, write $qAT^{3+(\gamma/2)}$ = B (a constant).

Therefore, the expression becomes: $I = B\, e^{-E_g/kT}\left(e^{qV/kT} - 1\right)$

Since we will perform experiment upto maximum 120°C, and the voltage will be of the order of few hundreds of millivolts (not exceeding 0.5 V), the exponential term in $\left(e^{qV/kT} - 1\right)$ dominates.

Hence the final-expression that we will work with is $I = B\, e^{-E_g/kT}\left(e^{qV/kT}\right)$

Note, in this expression the current is held constant, and B is practically independent of temperature for the range of interest in this experiment.

(5) Implementing the final-expression for determining the band-gap of semiconductor used for making the homojunction diode.

Note: You must have completed the Task #1 to #3 before coming to the laboratory for doing this part of the experiment. Task #1 to #3 will also be part of the laboratory-report.

Task #1) Rearrange and convert the expression $I = B\, e^{-E_g/kT}\left(e^{qV/kT}\right)$ to obtain a linear relation between Forward-bias (V) and temperature.

Task #2) Analyse the linear relation to decide how you will determine band-gap from the data-points obtained from the measurement of forward-bias vs. temperature for a fixed forward-current.

Task #3) Make a sketch indicating the electrical connections between various components necessary for this part of the experiment; you will be given following equipments for the experiment:

(1) A p-n diode (1N4148 by NXP Semiconductors founded by Philips)
Normally it would have been already placed into the custom-modified set-up. You may request TA to show another (identical) diode to you. Removing the diode from the set-up and putting it back again, will consume the limited laboratory time you have.

(1) A current source
(2) A multimeter
(3) An oven to heat the diode.
(4) Cables to make electrical connections; see appendix 1.

Task #4) Carryout the measurements and collect data points. See note below:

(a) Have the connections checked by TA before proceeding. Wrong connections will damage the instruments.
(b) The forward current will be fixed at 50 m Amp.
(c) Contact TA for help with heating the oven in which diode has been placed. TA will help you in taking the oven to highest temperature which is 120°C. Important: The existing arrangement to heat the oven doesn't have any safety arrangement to impose upper bound on the oven temperature. The only option at present to prevent the oven from going to very high temperature where it can damage the diode and itself is to shut the power supply as soon as temperature reaches 110°C. The temperature will shoot-up to ~ 120°C.
(d) Once the oven reaches at 110°C, the power-supply to it will be shut-down; the temperature will shoot-up to ~ 120°C. Record the readings that you decided in Task#2 above as the oven cools down. Take first point at 110°C and then for every temperature at 10°C difference; the last reading will be at 40°C. Note the oven cools down pretty quick when at high temperature so be alert. Any error in the temperature reading will affect your final value for the band-gap.

Task #5)

(a) Plot the data-points and determine the band-gap. The diode is made of silicon. Match the value you obtained with that available in the standard literature for silicon.
(b) Show that for the voltage and temperature range the term $e^{qV/kT}$ was much larger than 1 in order to be able to ignore it from the expression $(e^{qV/kT}-1)$.

--------------------------------------End of Part A---

Part B

(1) Objective

Determine dopant concentration in a semiconductor as a function of depth using capacitance-voltage characteristics of a Schottky-diode.

(2) Technique used

Capacitance – voltage (C-V) measurement

(3) Theoretical background

Metal-semiconductor junctions (contacts) can be of two types as far as the directionality of current-flow (charge-flow) across the junction is considered: (a) Ohmic contact in which charge-carriers can flow across the junction with ease in both the directions upon application of an external bias; (b) Schottky contacts in which for certain direction of the polarity of external-bias the charge-carriers can flow easily across the junction in one direction, while for the opposite polarity of external-bias the charge-carriers experience a barrier and thus cannot flow in the opposite direction. The schematics and plots shown in *figures 7 & 8* below indicate the difference in these two-types of metal-semiconductor junctions.

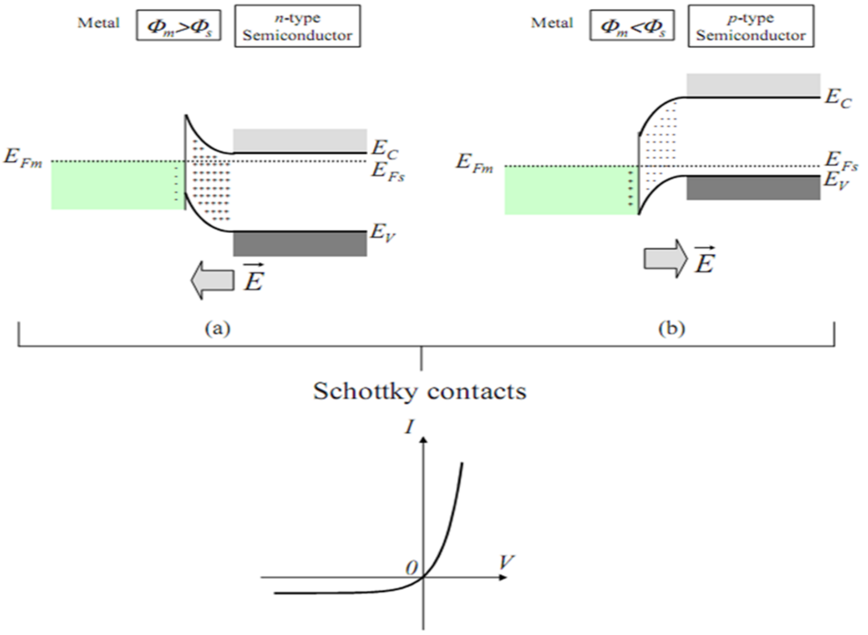


Fig. 9.24. These two of the four possible metal-semiconductor junction configurations lead to a Schottky contact: (a) $\Phi_m>\Phi_s$ and n-type, (b) $\Phi_m<\Phi_s$ and p-type. A Schottky contact is obtained in each case because the majority carriers in the semiconductor experience a potential barrier which prevents their free movement across the metal-semiconductor junction and therefore as shown at the bottom of the figure, the I-V characteristic shows rectifying behavior.

Figure: 7

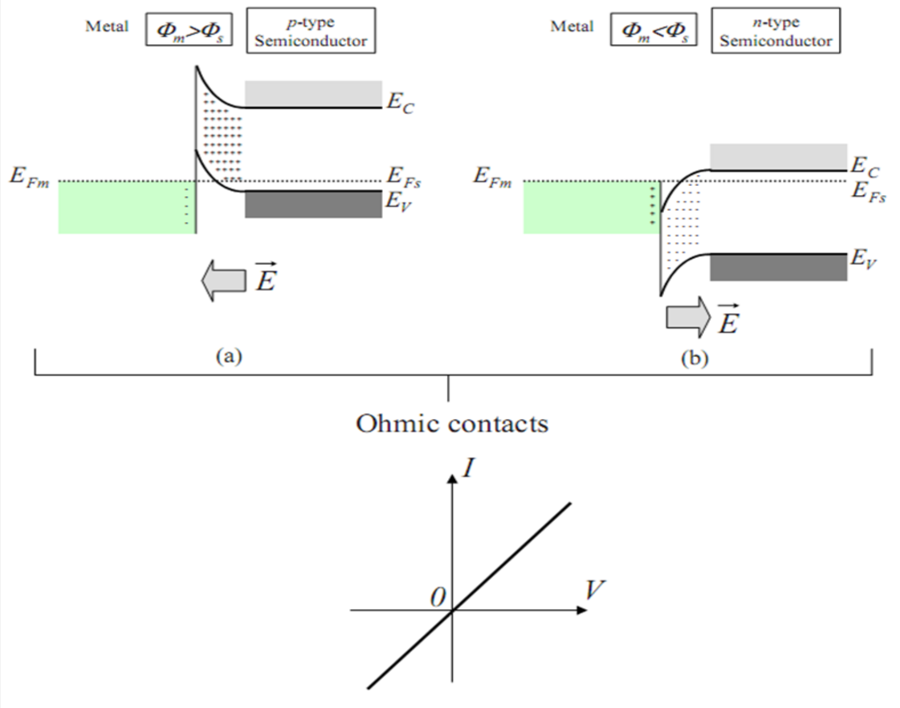
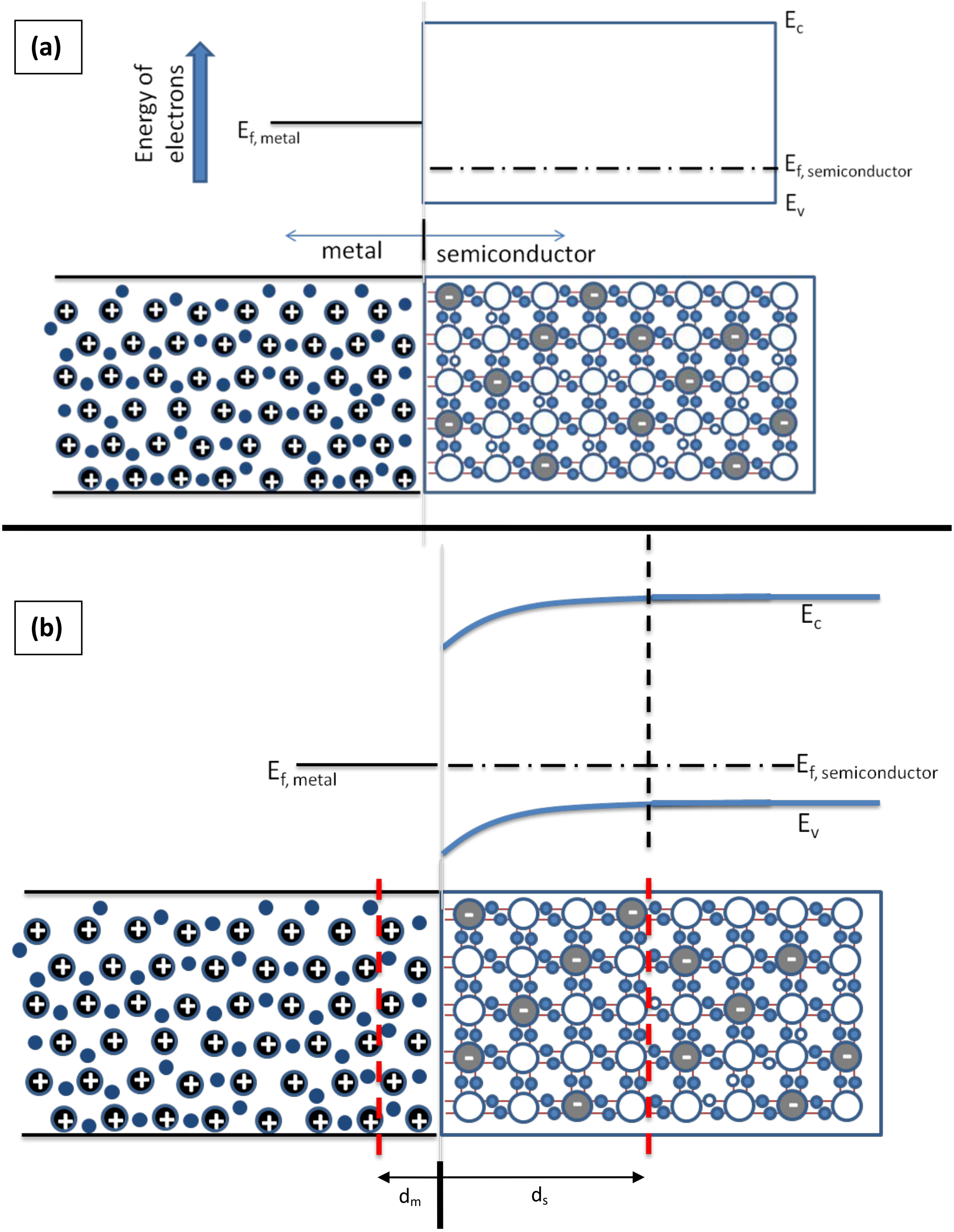


Fig. 9.25. These two of the four possible metal-semiconductor junction configurations lead to an ohmic contact: (a) $\Phi_m > \Phi_s$ and p-type, (b) $\Phi_m < \Phi_s$ and n-type. Unlike the configurations shown in Fig. 9.24, the energy band profiles here are such that the majority carriers in the semiconductor can move across the metal-semiconductor junction without experiencing a potential barrier and therefore as shown at the bottom of the figure, the I-V characteristic shows ohmic behavior.

Figure: 8

In this part of the experiment we will be using a metal-semiconductor junction device which shows Schottky behaviour. Let us first understand the depletion region, the capacitance associated with this depletion region, and its variation with reverse-bias. This will help us understand how the capacitance-voltage characteristics of a Schottky-diode can provide us dopant-concentration vs. depth information. Following discussion on a metal-semiconductor Schottky-junction device assumes a p-type semiconductor. When a metal having Fermi-level above that of semiconductor makes an electrical contact with this semiconductor, as shown in the *figure 9(a)* below, because the Fermi-energy level in metal is high compared to that in the semiconductor, electrons will *diffuse* from metal into the semiconductor. As shown in *figure 9(b)* these diffusing electrons will combine with holes in the semiconductor near the interface. Note that due to uniform distribution of holes (mobile charge carriers) and negatively charged acceptors (immobile charge carriers) the semiconductor is electrically neutral; however, as the electrons diffusing from metal into the semiconductor combine with holes, the negatively charged acceptor ions are left behind and because of these ions the region near the junction becomes negatively charged. Also, as the electrons diffuse out from metal, the positively charged metal-ions are left behind. Thus, in overall, there is a build-up of negative charge on the semiconductor



Practically ***d_m*** is/remains negligibly small compared to ***d_s***

Figure: 9

side of the interface, and positive-charge on the metal-side of the interface. *Note that unlike electrons and holes, these charges that build-up on the two sides of interface are immobile.* Due to build-up of charges on the two sides of interface an electric-field is established which in this case would have direction from metal (positive immobile charge) to semiconductor (negative immobile charge). This electric-field exerts electrostatic attraction force on the diffusing electrons, and this force is directed from semiconductor to metal, exactly opposite to the direction of diffusion which in this case is from metal to semiconductor. In the beginning the electric field doesn't exist, however, as the diffusion continues across the junction, the immobile charges gradually build-up on the two sides of interface giving rise to an electric-field. When the two opposite forces experienced by the electrons due to electric-potential difference (due to built-in electric-field) and the difference in chemical-potential become equal the flow of charge-carriers across the junction stops. The region in the semiconductor near the interface where there are no holes (mobile charge) is called depletion-region or space-charge region. Note that at this stage the region on the two sides of interface resembles a parallel-plate capacitor, where one plate is metal and the other plate is a semiconductor. The semiconductor of depletion region is acting as dielectric between these two plates.

Above was the description of processes that take place when the system (metal-semiconductor) comes to a state of equilibrium after the contact between the two is established for the first time. The resulting build-up of depletion-region on the two sides of interface leads to corresponding capacitance. Now let us bring this system to non equilibrium state by reverse-biasing it as shown in *figure 10*; upon application of a reverse-bias the width of depletion region increases and for a given increase (V_1 to V_2)/decrease (V_2 to V_1) in the reverse-bias there is corresponding decrease/increase in the capacitance associated with this depletion region. Note that the capacitance is inversely proportional to the spacing between the two electrodes of a capacitor. By studying the change of capacitance with change in reverse-bias, dopant concentration can be obtained. To understand how it is done, let us observe the second schematic in *figure 10* in which a reverse-bias = V_1 (a DC-bias) has been applied such that the boundary between the depletion region and the neutral semiconductor lies at depth = w inside the semiconductor. Now consider a small-amplitude ac signal superimposed on this DC bias because of which the schottky-diode experiences a reverse bias varying between $\mathbf{V_1 - \Delta V}$ and $\mathbf{V_1 + \Delta V}$. Change in the bias (dV) on a capacitor leads to corresponding change in the stored charge on that capacitor, which in the present case is achieved through the change in the amount of immobile charge (dQ_s) that is part of the depletion region. Therefore, by using Q = CV relation, following can be written :

$$C = \frac{dQ_m}{dV} = -\frac{dQ_s}{dV}$$

where Q_m and Q_s are the metal and semiconductor charges

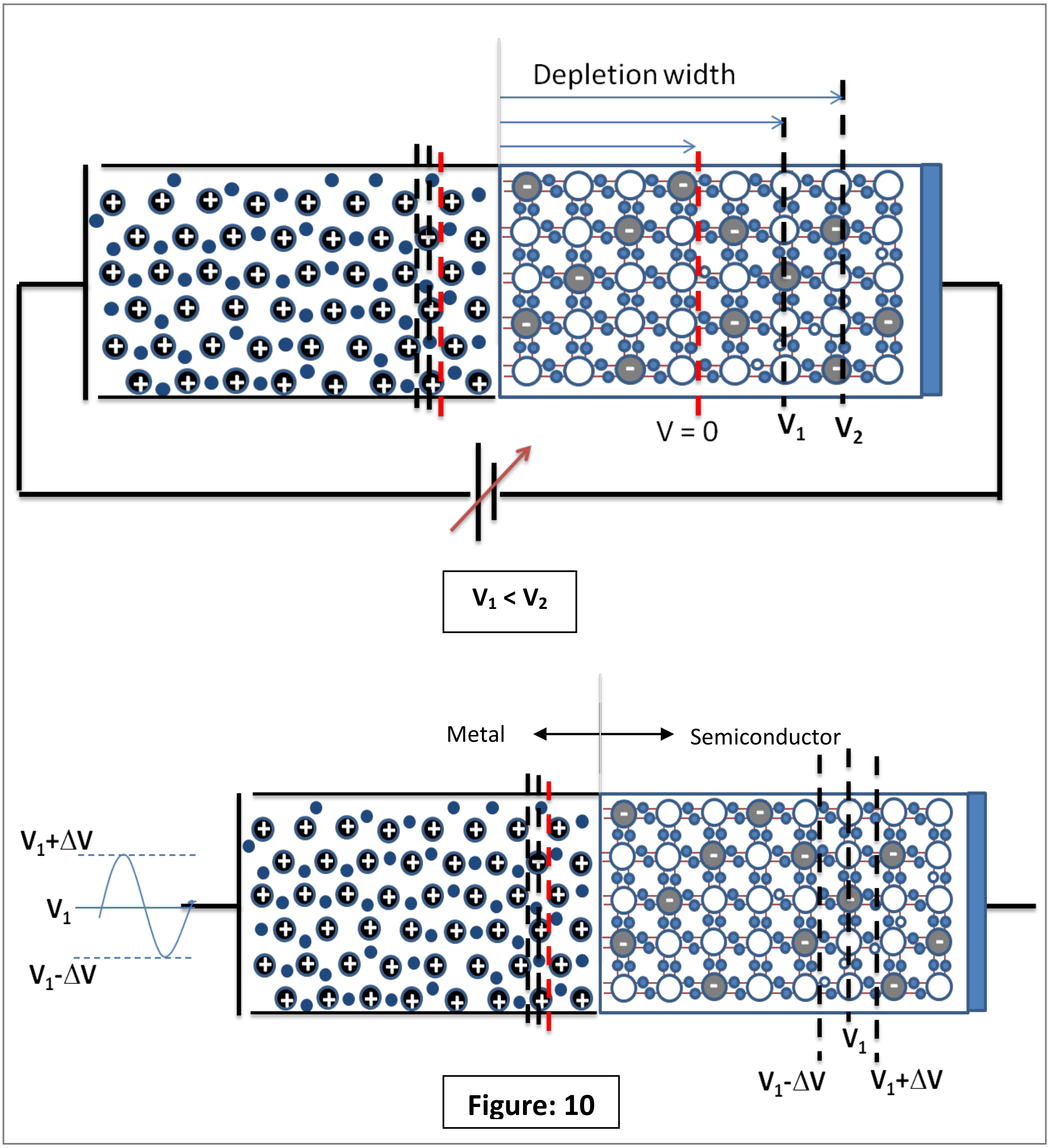


Figure: 10

However, as shown in the figure 10, the change in the stored charge on that capacitor also requires the width of the depletion region to vary from W_1 - ΔW and $W_1 + \Delta W$, and hence following expression can be written:

$$C = -\frac{dQ_s}{dV} = qA\frac{d}{dV}\int_0^W N_A\,dx = qAN_A(W)\frac{dW}{dV}$$

From this expression you can see that the measured capacitance depends on the dopant concentration $N_A(w)$ at the location of depletion-region – neutral region boundary at depth *w*. However, the relation is not so straightforward because from the same expression we see that the capacitance is also dependent on ***dw/dV***. Let us try to replace this later term which itself is dependent on the dopant concentration. Using the standard expression for capacitance and differencing it with the voltage (reverse-bias) following expression is obtained:

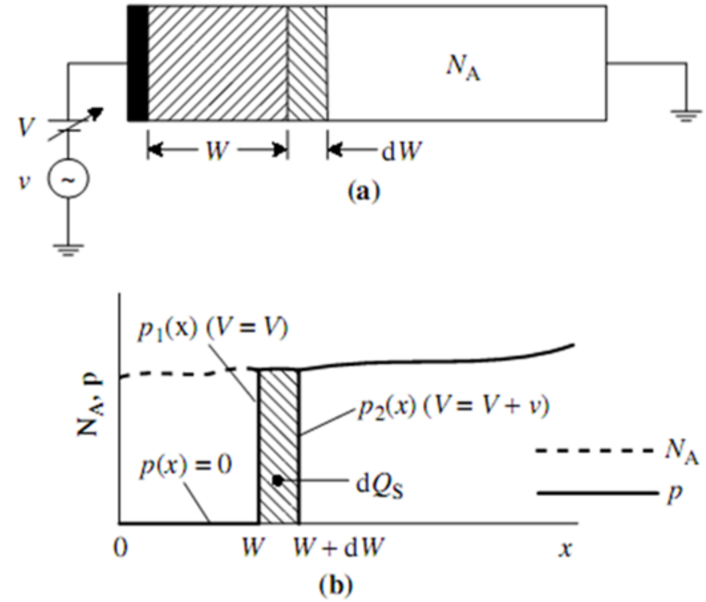


Fig. 2.1 (a) A reverse-biased Schottky diode, and (b) the doping density and majority carrier density profiles in the depletion approximation.

Figure: 11

$$C = \frac{K_s \varepsilon_o A}{w}$$

After differentiating with respect to reverse-bias

$$\frac{dC}{dV} = -\frac{K_s \varepsilon_o A}{w^2}\frac{dw}{dV} \quad \Longrightarrow \quad \frac{dw}{dV} = -\frac{w^2}{K_s \varepsilon_o A}\frac{dC}{dV}$$

Substituting the expression for dw/dV from above into the expression relating the capacitance and dopant-concentration above, the following final expression is obtained after some rearrangement:

$$N_A(W) = -\frac{C^3}{qK_s\varepsilon_o A^2\, dC/dV} = \frac{2}{qK_s\varepsilon_o A^2 d(1/C^2)/dV}$$

This expression indicates that by measuring the slop of the plot for ($1/C^2$) vs. reverse-bias (V) at a particular value of reverse-bias the dopant concentration can be obtained. Since the reverse-bias also governs the width ***w*** of depletion region**,** the dopant-concentration measured corresponding to a particular reverse-bias is also the dopant-concentration for a particular depth inside the semiconductor. This width (w) corresponding to a given reverse-bias can be calculated by using the expression

$C = \frac{K_s\varepsilon_o A}{w}$ for which we already have determined capacitance through experiment.

K_s; 11.82

ε_o; (Permitivity of free space) 8.85 x 10^{-12} F/m

(6) Implementing the final-expression for determining the dopant-concentration as a function of depth in the semiconductor that has been used for making the schottky-diode.

Note: You must have completed the Task #1 and #2 before coming to the lab for doing this part of the experiment. Task #1 to #2 will also be part of the laboratory-report.

Task 1

Use the final expression for N(w), and decide what parameters you will be controlling during the experiment, and what parameters you will be measuring.

Task -2

Make a sketch indicating the electrical connections between the various components for the experiment; you will be given following equipments for the experiment:

(2) A Schottky-diode (1N5817 Diode by STMicroelectronics)
(3) A voltage source
(4) A multimeter
(5) A capacitance-meter
(6) Cables to make electrical connections

See, appendix 2 for correct way of electrically connecting the instruments.

Task -3

Carryout the measurement and collect data points. See note below:

(a) For reverse biasing the diode you will have to decide the direction of the bias to be applied to the diode. For this, connect the diode to a voltage-source and measure the current through the diode for 3-4 values of voltages. Now change the polarity of bias on the diode and again carryout measurement for 3 – 4 values of voltages. Use the I-V plot shown at the beginning of section B to decide what polarity would cause reverse-biasing on the diode. Once you decide the polarity, make final connections, and then have the connections checked by TA before proceeding. Wrong connections will damage the instruments.

Do not exceed the forward-bias to large extent because in forward-bias current increases quickly and it could damage the diode permanently. See the I-V characteristic of the schottky-diode you are using is given in Figure 7.

(b) For reverse-biasing do not go exceed the bias too much, else there will be electrical break-down and current will rise very rapidly. It could be damaging for the diode.

(c) Once the connections have been checked by TA for its correctness, make measurements for the parameters that you have decided in Task #1 above.

Task -4

Using the final expression we arrived at in section 5, and the data points (C vs. voltage), determine dopant concentration as a function of depth inside the semiconductor. Calculate area of cross-section for the diode using its diameter to be equal to **~0.8 mm.**

----------------------------End of Part B---

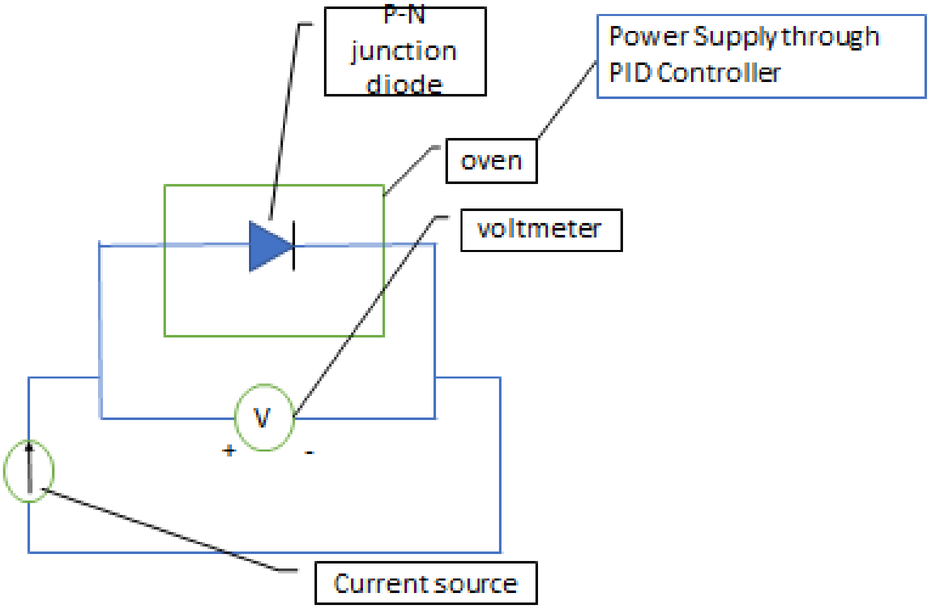
References:

(1) Semiconductor Materials and Device Characterization, D. K. Schroder, John Wiley & Sons, 2006.

(2) Semiconductor Devices: Physics and Technology, S. M. Sze, and M. K. Lee, John Wiley & Sons, INC. 2010.

Appendix -1

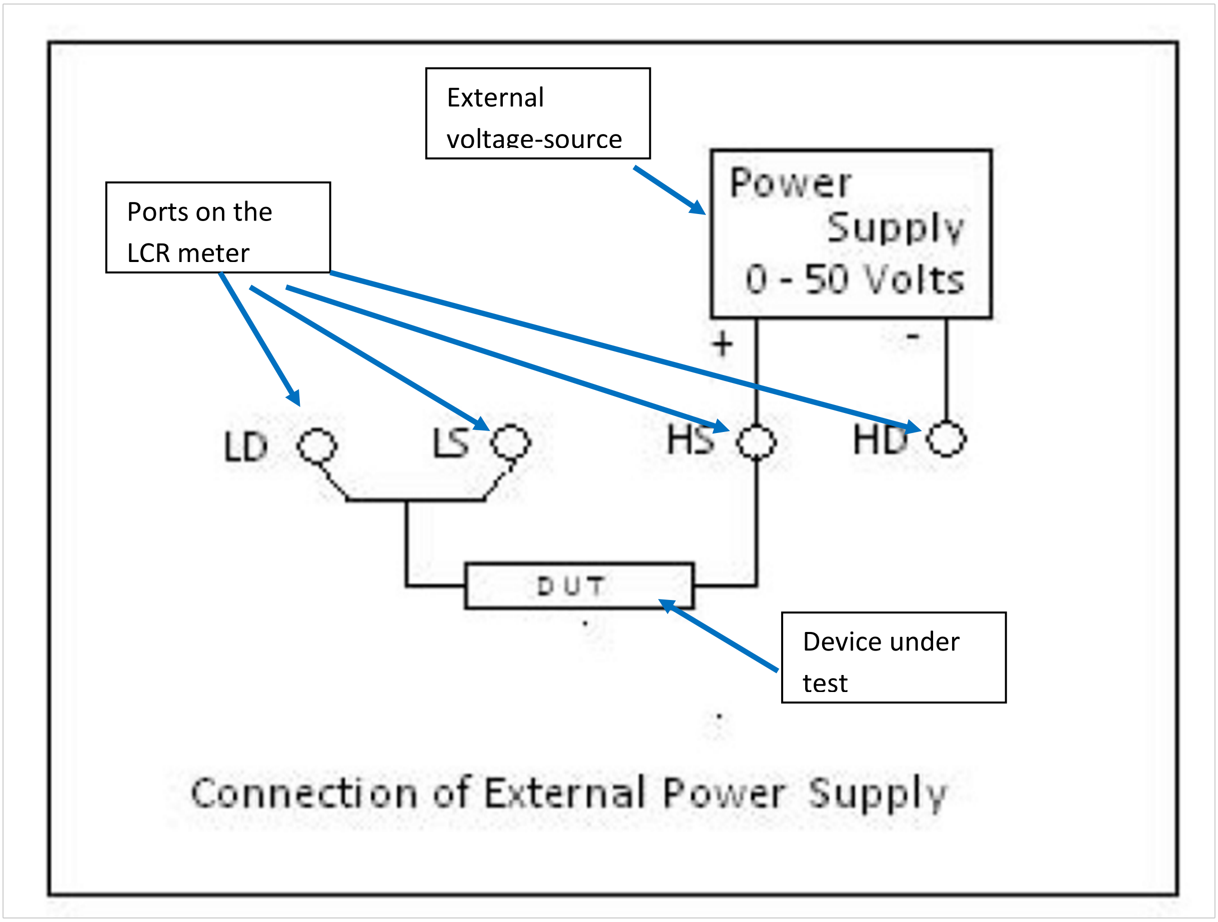
Following schematic shows connection scheme to be followed for the *Part A* of this experiment for measuring resistance of a device using the voltmeter and constant current source (source meter) that you have been provided for this experiment.



PART A

Appendix -2

Following schematic shows connection scheme to be followed for the *Part b* of this experiment for measuring capacitance of a device using the LCR meter that you have been provided for this experiment.



EXPERIMENT-7

Determination of Ferroelectric Phase Transition in KNO_3

Aim:

Observation of a ferroelectric phase transition in potassium nitrate and measurement of its transition temperature.

Background:

There are at least three systems in nature that exhibit hysteretic responses to driving forces: ferromagnets, ferroelectrics, and ferroelastics. The latter are materials that have hysteresis in their stress–strain relationships. Of the three systems, only ferromagnets are usually the subject of undergraduate laboratory experiments. A ferroelectric is a material in which an electric dipole moment is present even in the absence of an external field. This typically occurs as a result of a change in the crystal structure so that the centers of positive and negative charge in the crystal do not coincide. Ferroelectric materials undergo a phase transition across a characteristics temperature called as Curie temperature, T_c. Above this temperature, the material's structure is centrosymmetric (crystal with a centre of symmetry) and material is paraelectric in nature i.e. there is a linear relation between polarization of the material (dipole moment per unit volume) and electric field. Upon cooling below T_c, the material's structure changes to a noncentrosymmetric structure which is also characterized by the presence of a ferroelectric hysteresis loop, as shown below.

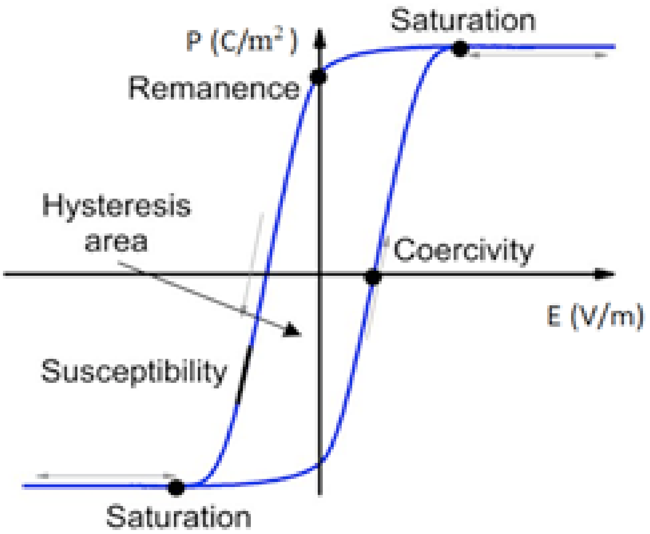


Fig. 1: A typical ferroelectric hysteresis loop

Normally it is difficult to demonstrate ferroelectricity in the classroom laboratory as the coercive fields of most materials are of the order of kV/cm, making experiments on bulk ferroelectrics potentially dangerous and unsuitable for students. Ferroelectrics in thin film form, on the other hand, may be switched with a few volts and there is now both production of and research on nonvolatile memories based on ferroelectric thin films. Typically, however, thin films are deposited in expensive chemical vapor deposition or pulsed-laser deposition machines, making the fabrication of thin films by students as part of a teaching experiment impractical. In this experiment the students can make and characterize a ferroelectric thin film capacitor using an inexpensive material Potassium nitrate. It is a material with a ferroelectric phase (Phase III in the figure below) which in bulk form is stable only between 115 and 125 °C, but is metastable at room temperature. It has been found that when KNO_3 is made as a thin film, the lower temperature limit of the ferroelectric phase is lowered, and it can be stable at room temperature.

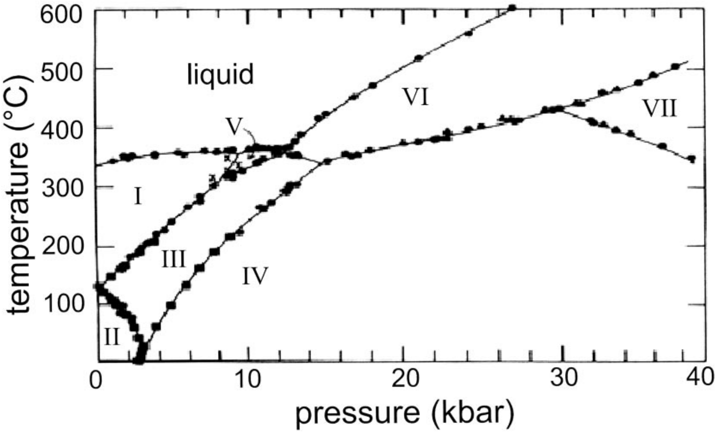


Fig. 2: Phase diagram for bulk KNO_3 with temperature as a function of hydrostatic pressure

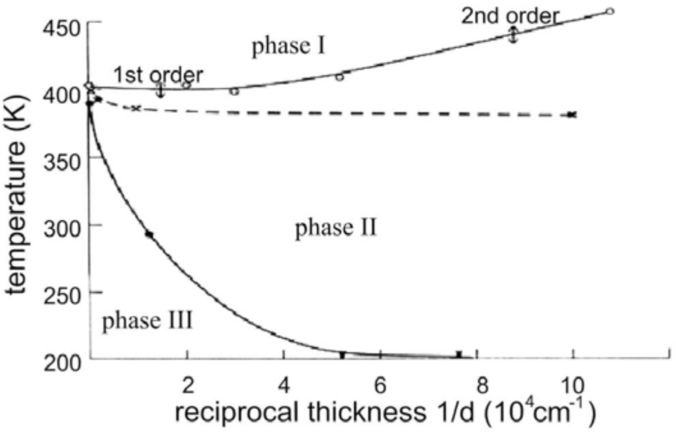


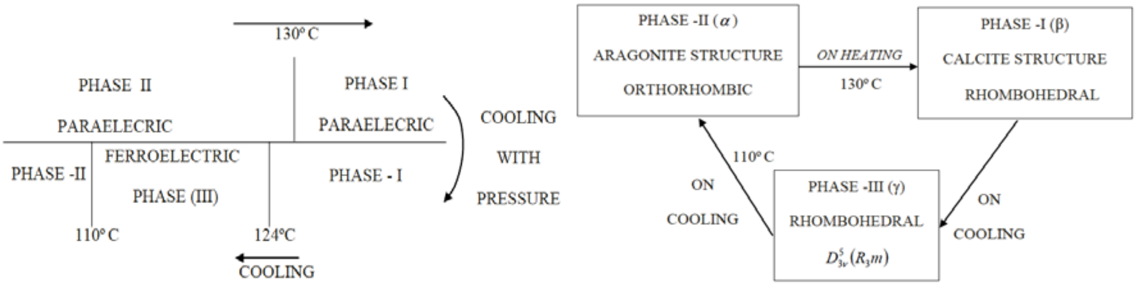
Fig. 3: Phase diagram for KNO_3 thin films with temperature as a function of reciprocal thickness.

Phase diagrams for bulk KNO_3 and for thin films are shown in Figs. 2 and 3, respectively. Figure (4a) and (4b) also shows the transition between different phases upon heating or cooling. Whereas, crystallographic data for the three phases of KNO_3 are listed in table 3. In bulk the phase transition is a re-entrant phase transition, i.e., it can be reached only on cooling and not by heating. This is because the ferroelectric phase is narrower than the thermal hysteresis.

Table 1: Crystallographic data for the three phases of KNO_3

Phase of KNO_3	**Temperature (°C)**	**Unit –cell data (Å)**			**Crystal structure**	**Space group**
		a	b	C		
Phase II	19	5.414	9.164	6.431	Orthorhombic	P_{nma}
Phase I	128	5.423	5.423	9.638	Rhombohedral (α_R= 73° 50′)	$R\bar{3}m$
Phase III	110	5.430	5.430	9.095	Rhombohedral (α_R= 76° 56′)	R3m

Potassium nitrate is not used for commercial applications because the challenges of fabricating capacitors have proven too difficult. KNO_3 readily absorbs water from the atmosphere, thereby severely degrading its ferroelectric properties.



a) b)

Fig. 4: Phase transition in KNO_3 upon heating/cooling

The main materials used today for ferroelectric memories are lead zirconate titanate and strontium bismuth tantalate. Because potassium nitrate melts at about 330°C it is quite straightforward to melt the powder and then cool it to form a thin film in which hysteresis properties may be measured with an acceptably low voltage. In this laboratory experiment, we fabricate and measure the properties of a KNO_3 capacitor by thermally cycling the material on a hot plate.

Sawyer-Tower Circuit:

The standard circuit used to measure a ferroelectric hysteresis loop is the Sawyer-Tower circuit. Our implementation of this circuit is shown in Fig. 4.

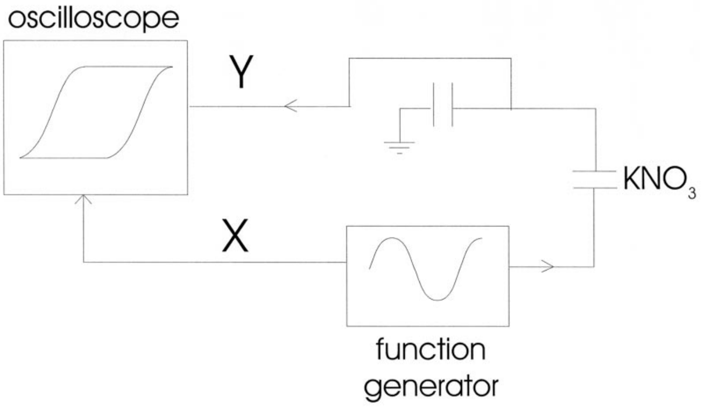


Fig. 5: Sawyer-Tower circuit as implemented in the experimental setup described here.

By measuring the potential V across a standard capacitor in series with the KNO_3 film one can determine the charge Q on the KNO_3 capacitor using Q=CV. When two capacitors are in series the charge on each capacitor must be the same (in an ideal capacitive circuit no current flows), so the electric charges on the standard capacitor and the KNO_3 capacitor are the same. As the capacitance C of the standard capacitor is known we are able to calculate Q from the magnitude of the voltage signal we measure at the standard capacitor.

We display the signal applied to the material as the X signal of an X-Y trace on an oscilloscope. Most of the voltage drops across the KNO_3 capacitor because we have selected a high value of capacitance for the standard capacitor, so we can consider the X signal to represent the voltage across the sample. The Y signal is proportional to the charge on the KNO_3 capacitor.

If this technique were used on an ordinary linear dielectric one would expect a linear response (a straight line on the x-y display), as the polarization is directly proportional to the field applied. In practice there is some opening of the loop, which is due to dielectric loss. In a ferroelectric there is a remnant polarization, i.e., the polarization charge remains aligned in the direction it was poled by the applied field even after this field has been removed. The electrical polarization characteristics of the capacitor thus depend on the history of the field that is applied to it and hence it displays hysteresis.

Requirements for the experiment:

A. Electrical equipment

1. A basic oscilloscope. It must be capable of operating in X-Y mode. It only needs to be capable of operating at low frequencies i.e.100–1000 Hz_.
2. A signal generator. It should be capable of producing sine waves of 15-V amplitude. Frequencies in the range of 100–1000 Hz give the best hysteresis measurements.
3. Hotplate. It should be capable of heating the sample to at least 350 °C.
4. Thermocouple. A thermocouple is used to measure the temperature of the capacitor during the experiment.

5. Test box, which is assembled with a transistor, an audio transformer which simply provides more switching voltage.

(There are two outputs from the test box. One is the input signal generated by the signal generator after amplification. The other is the signal across the standard capacitor. These are connected to the X and Y channels of the oscilloscope, respectively.)

The standard circuit used to measure a ferroelectric hysteresis loop is the Sawyer-Tower circuit as shown above.

B. Other requirements

- KNO_3 powder
- Metal sheeting, e.g., aluminum or copper cut into small squares
- Thumbtacks
- BNC cables for interconnection
- Insulated gloves,
- Glass microscope slides

Description of the electric cable connections:

1. Connect the output signal connectors on the test box marked X and Y to the X and Y channels of the oscilloscope using BNC cables.
2. Connect the sensor (wires from Thumbtrack and plate) to the knob of the test box using the appropriate port.
3. Connect the output of the function generator to the test box at the port marked “Signal in”
4. Switch on the oscilloscope keeping it in dual mode with Time base.
5. Switch on the function generator and adjust the output to sine wave with a frequency anywhere between 100-500Hz. Adjust the amplitude so that X signal has an amplitude of about 25V.
6. Press the XY botton of oscilloscope.

Brief Description of the Experimental procedure

1. KNO_3 is highly hygroscopic and hence readily absorbs the water from the atmosphere, thereby severely degrading its ferroelectric properties. Therefore it should be dried before use. Heat KNO_3 in an oven for 1hr at $100^{o}C$. You may be provided a preheated material.
2. Potassium nitrate melts at about 330°C and so it is quite straightforward to melt the powder on a hot plate and then be able to cool it to form a thin film in which hysteresis properties may be measured with an acceptably low voltage.
3. Take a square, thin aluminum or copper sheet that acts as a bottom electrode. A small tab on one corner is bent up to allow easy electrical contact with an alligator clip.
4. Use microscope slides to insulate the metal sheet electrically from the hot plate.
5. A thermocouple is inserted to measure the temperature.
6. About six to eight thumbtacks should be placed on the powder. We found that upon melting of the KNO_3, thumbtacks would automatically form a capacitor of suitable thickness; they are also easy to connect to the test box with an alligator clip

7. Once the experiment has been set up, the heater should be turned on until the KNO_3 is completely molten. At this point the heater may be turned off and the sample is allowed to cool. The alligator clips may be attached, one to the bottom electrode and the other to any of the thumbtacks.
8. If at this point a signal is applied, the result on the oscilloscope will be a loop, essentially a linear response opened up by dielectric loss.
9. As the capacitor goes through the phase transition, the loop will change dramatically and become very square (Note the temperature at which shape of the loop starts changing at upto what temperature the the shape again change from square shape.)
10. For 9 and 10, to achieve a plot with good aspect ratio, you may need to change the Y-scale on the oscilloscope.
11. The nature of the plots which you need to draw should be something like as shown below. X-axis represents the voltage while y-axis represents the charge stored which can be converted into polarization which is nothing but charge per unit area.
12. Temperature at which the shape of the loop changes can vary depending on experiment but should be between 100-120°C.

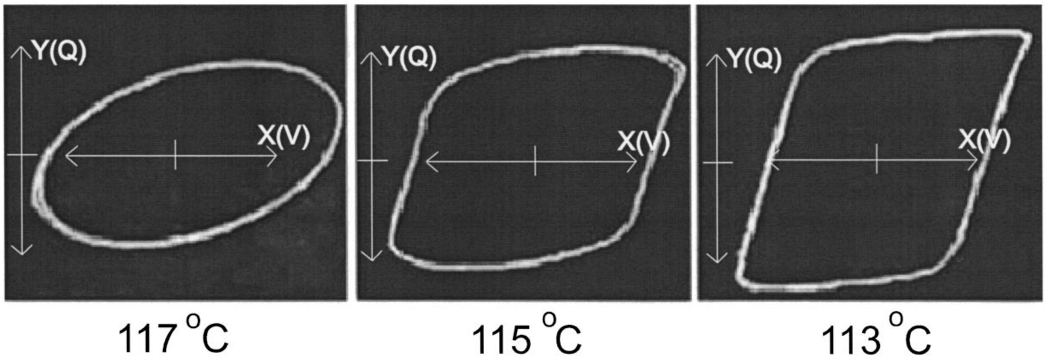


Fig.6: Schematic representation of phase change

Expectations from the Students:

i. Learn what a ferroelectric material is?
ii. Why do we use KNO_3 for this test and why do we need to melt it to make the measurement?
iii. What happens at the ferroelectric transition?
iv. What do shapes of the loops below and above the transition signify?
v. What could be other ways of observing similar transition for any material at low voltages?

References:

1. M. Dawber, I. Farnan, and J. F. Scott, A classroom experiment to demonstrate ferroelectric hysteresis, American Journal of Physics, 71, 819 (2003); doi: 10.1119/1.1561271
2. A.J. Dekker, Solid State Physics, Macmillan & Company

EXPERIMENT-8

Solar Cell Fabrication and Characterization

Aim: Fabrication and characterization of an organic photovoltaic cell

Background:

Organic photovoltaic cells use organic semiconductors for charge generation and transport. The devices using semiconducting polymers are light weight, mechanically flexible, and can be produced at low cost. The use of printing technology and thin plastic substrates for roll-to- roll processing are catching attention for portable power source. The limiting factors are their low efficiency and short life time.

The conversion in to electrical energy is carried out in two steps generation and collection of charge carriers. Figure.1 shows the structure of the typical organic solar cell. . Organic Solar Cell generally consists of an organic layer, anode and a cathode. Organic layer, in this experiment is a blend of P3HT and PCBM, helps in the generation of excitons (a bound state of electron and hole) by absorbing light energy. These excitons gets seperated into electron and hole at the interface of P3HT and PCBM because of the difference in HOMO and LUMO levels of these materials. As a result electrons will go from P3HT to PCBM and holes will go from PCBM to P3HT. These seperated electrons and holes will move towards cathode and anode respectivly and creates electric current. Cathode and anode work function will play important role in extacting electrons and holes. To understand the mechanism of the energy conversion in OSC, six steps are described below.

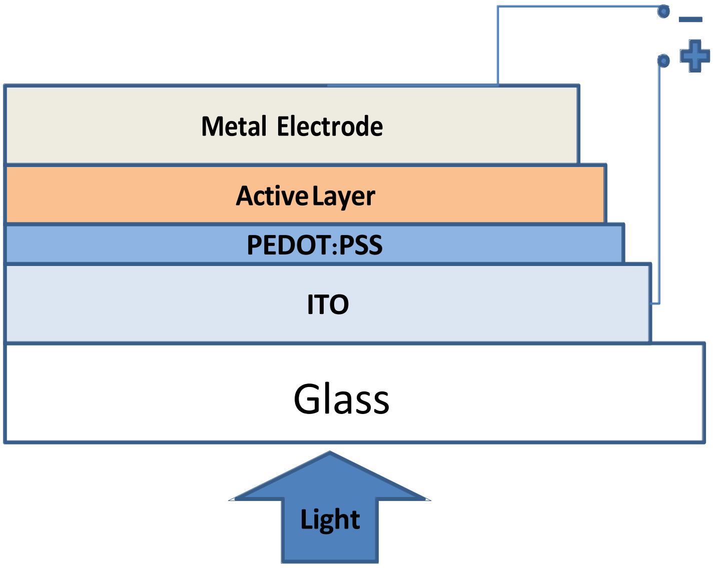


Figure 1: structure of organic solar cell

(1) Absorption of photon: - The process of energy conversion is initiated with the absorption of incident radiation by the active material. When the photon is incident on the material, then it gets either scattered or absorbed (if $h\upsilon \geq E_g$). E_g is defined as the difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. The incident photon generates electron-hole pairs largely in the p-type material via electron transition from π-HOMO to π^* -LUMO bands. The degree of absorption depends on the absorption coefficient and thickness of the material.

The absorption is limited by several factors. Since the refractive index of organic material is low so losses at air-active layer interface due to reflection is negligible. However the critical factors are mismatch between solar spectrum, absorption spectrum of the material and thickness of the active layer. The absorption coefficients of organic materials is high ($\sim 10^5$ cm^{-1}) still active layer has to be sufficiently thick perceptible absorption. The absorbed intensity (I) is given by

$$I = I_o(1-e^{-\alpha x})$$

Where, I_o is the intensity of incident light, α is the absorption coefficient, and x is the thickness of the active material.

(2) Exciton Formation:- Photo excitation leads to formation of a neutral entity (bound electron-hole pair or exciton) of finite life time. The binding energy of the exciton is around 0.1-0.2 eV.

(3) Exciton Diffusion:- Exciton diffuses through the organic material via Forster (long range) or Dexter mechanism i.e between adjacent molecules. Due to finite life time of exciton, its dissociation length is very small ~ 10-20 nm.

(4) Exciton dissociation:- The dissociation of exciton in to free carriers needs energy which is provided by internal electric field at the donor- acceptor interface.

(5) Charge transport:- The separate charges travel towards the electrode by hoping process in organic materials. Some charges also get trapped and are unable to reach electrode.

(6) Charge collection:- For this work function of the electrodes need to satisfy following conditions

$(E_F)_{cathode} < (E_{LUMO})_{acceptor}$

$(E_F)_{anode} > (E_{LUMO})_{donor}$

There is an inherent trade off between absorption and exciton diffusion. For getting high absorption we need high thickness while this increased thickness affects the exciton separation and transport of charges. Therefore in practical situation active layer thickness has to be optimized Important Parameters:-

Short Circuit current Density (J_{sc}):-

The current flowing in the external circuit under zero bias condition in a solar cell is called short circuit current. However, J_{sc} have more significance than I_{sc} and is represented by J_{sc}. It depends on the nature of semiconductor i.e. mobility, life time, diffusion length, electrodes and intensity of incident light.

Open Circuit Voltage (V_{oc}):-

It is the voltage under open circuit condition, i.e. when the current is zero. For single layer devices it is defined by the difference in the work function of electrodes, whereas in bi layer and bulk heterojunction Voc depends on the difference between the energy of $donor_{(HOMO)}$ and $acceptor_{(LUMO)}$ besides the difference between the work functions of the electrodes.

Fill Factor:-

It is defined as the ratio of maximum power from a solar cell to the product of V_{oc} and I_{sc}. It is given by the area of biggest rectangle fitting in 4th quadrant of the I-V curve (fig. 2). Physically it amounts to maximum power that can be drawn from the solar cell. Notice that the power extracted at Voc and Jsc is zero. Fill factor depends series and shunt resistances .

$$FF = \frac{Vmpp * Impp}{Voc * Isc}$$

High series resisitance flattens the J-V curve and hence reduces the short circuit current where as low shunt resistance is responsible for the leakage current and so causes reduction in open circuit voltage.

Equivalent Circuit Model:-

It consists of a current source, a diode ,two resistances one in parallel(called shunt R_{sh}) and one in series(called series R_s) . For an ideal solar cell, Rsh=∞ and R_s= 0. The equivalent circuit of typicalsolar cell is shown in figure 3

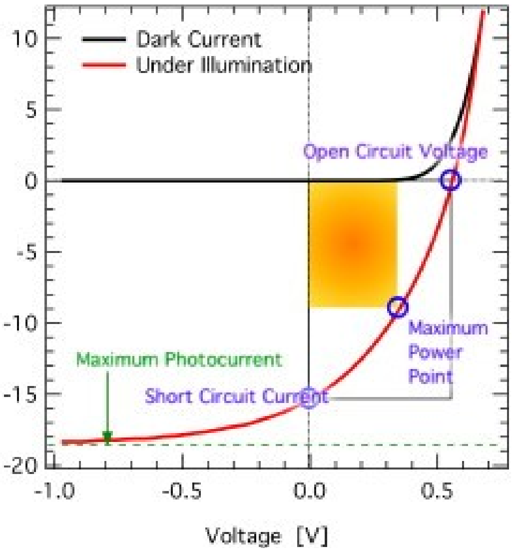


Figure 2: Typical I-V curve of a solar cell

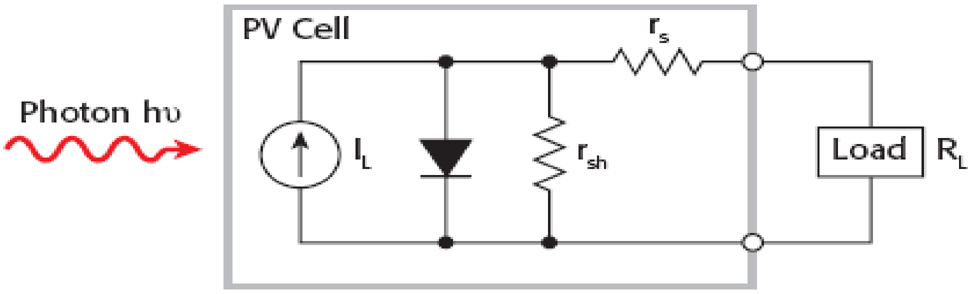


Figure 3: Equivalent circuit model of solar cell

Series resistance(R_s):-

Series resistance arises from resistance of the cell itself. It takes into account conductivity of charge carriers and hence mobility of charge carriers in respective transport medium. It can be calculated from inverse slope of the IV characteristic around V_{oc}. Mathematically it can be given by

$$Rs = \left[\frac{dI}{dV}\right]^{-} \quad Voc$$

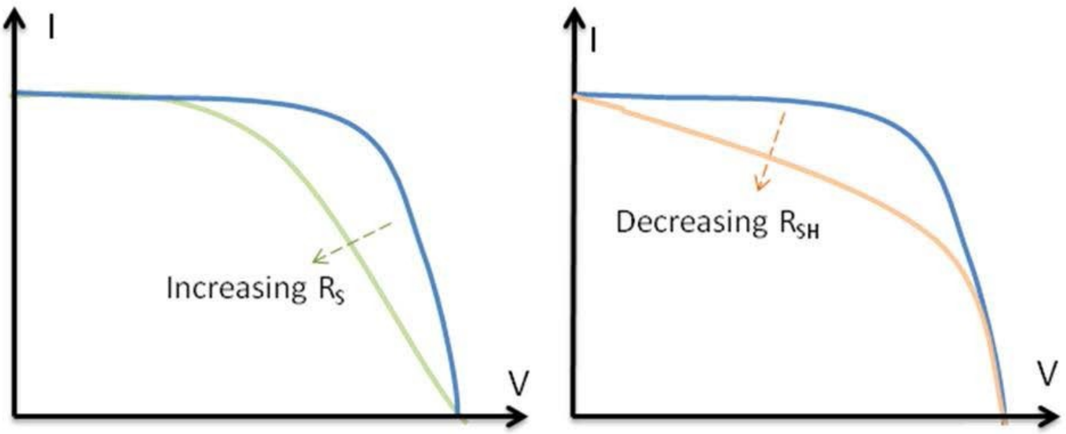
For good Solar cell, series resistance should be as low as possible. For an ideal solar cell it should be zero.

Shunt Resistance(R_{sh}):-

Shunt resisitance accounts for recombination losses of charge carriers.Its value can be calculated by inverse slope of IV curve near zero voltage.Mathematically it can be given by

$$Rsh = \left[\frac{dI}{dV}\right]^{-1} \quad V=0$$

Actually at low voltages diode does not conduct and hence the current is controlled by Rsh only. The higher shunt resistance is required for good solar cells. Ideally it should be infinite. Lower shunt resistance leads to lower Fill factor.



In an Ideal solar cell, current I is given by

$$I = I_L - I_D = I_L - I_o(e^{qV/kT} - 1)$$

Fig.4: Effect of R_s and R_{sh} on the performance of the solar cells[21]

Where Io is saturation current of diode, I_L is photo generated current, q is elemental charge, K is Boltzmann costant, T is cell temperature and V is measured cell Voltage (either applied or generated).

By incorporating Rs and Rsh, above equation gets modified to

$$I = I_L - I_D = I_L - I_o(e^{q(v+IRs)/\eta kT} - 1) - \frac{V+IRS}{Rsh}$$

Where η is ideality factor of diode.

Power Conversion Efficiency:- It is defined as ratio of total power output to total power of incident radiation, i.e. $\eta = \frac{Voc*Jsc*FF}{Pin}$

It involves three most important parameters Viz. J_{sc}, V_{oc} and FF. Generally η is represented as percentage rather than fraction.

For further reading http://pveducation.org/pvcdrom/introduction/solar-energy

Requirements for the experiment:

Materials:

1. ITO coated on glass as anode
2. PEDOT:PSS as Hole Transport layer (HTL)
3. P3HT:PCBM as absorbing layer
4. GaIn/Ag paste as cathode
5. DI water, chlorobenzene, acetone, methanol.

Equipment:

1. Sample holder
2. Multimeter & Diamond Cutter Pencil
3. Ultrasonicator
4. Nitrogen Gun
5. Spin coater
6. Hot plate or oven
7. Solar simulator set up.

Other requirement:

Beakers, soap solution, brush spatula, tweezers, syringe, filter, aluminium foil petridish, apron, gloves, mask, head cover, eye glasses, cotton swabs,

Brief Description of the Experimental procedure

Basic Fabrication Steps:

1. Cleaning of ITO coated, patterned glass substrates
2. Coating and annealing of HTL and active Layers
3. Deposition of cathode
4. Characterization

1. Cleaning of ITO coated, patterned glass substrates:

1. Wear safety equipment's (apron, gloves, mask, head cover, eye glasses).
2. Wash the equipments beakers, syringes, petridish, stand, tweezer and measuring cylinders with once with soap solution and thrice with DI water respectively. Put them in oven at 110°C. CHECK: This step may already have been performed before you come to the laboratory.
3. Turn ON the clean bench, if it is not already turned ON. Switch on the air blower from the switch located in front panel of the clean bench.
4. Check which side of substrate is conductive. Conductive side is ITO (anode). Then mark

the glass side, some number so that we can easily recognize the ITO side.

5. Wash patterned ITO substrates in soap solution with the help of a tooth brush and rinse them first in tap water and then in DI water. Place all the substrates in Teflon sample holder (figure 2).

Figure 1 Washing Substrate with soap and DI water

Figure 2 : Placing of substrates in Teflon sample holder.

6. Clean these substrates using ultrasonicating them in DI water, acetone. Make sure that substrate should be completely dipped in acetone. Put that beaker in ultrasonicator which should be on the clean bench. ATTENTION: water should be filled 2/3 of the height of ultrasonicator. Switch on the ultrasonicator by on/off button and set timer for ultrasonication. We can increase/decrease the time in the step of 5 minutes by pressing arrow up/ down button. Here we do ultrasonication for 10 minutes (figure 3 a and b)

Figure 3: (a) substrates placed in ultrasonicator (b) magnified view of front panal from where we can set time and temperature for ultrasonication.

7. Repeat step 6 for methanol and DI water. Dry the substrates by holding it with tweezer using drier. Keep these substrates in a petridish and place them in oven at a temperature slightly above 100^{o}C (approximately 100^{o}C) for 10 min, to evaporate any residual water.

8 Take out the substrates out of oven and let them cool before proceeding to the next step.

Coating and annealing of HTL and Active Layer

2(a). HTL Coating and Annealing

Preparation of PEDOT: PSS solution:

1. We place PEDOT: PSS (blue color liquid) bottle in refrigerator. Make sure that it will be kept outside 30 minutes prior to use so that solution of PEDOT: PSS cool down to room temperature.
2. Filter the solution before coating it with 0.46 micron filter.

Spin coating:

This technique is used to deposit thin films by using solution of the respective material. In this technique we pour an amount of the solutions on the substrates, which are then rotated at high speed in order to spread the liquid by centrifugal force. This procedure quickly evaporates the solvent and creates a uniform solid film whose thickness will depend on the speed rotation, solution viscosity and time of rotation.

Operation of spin coater:

We have a spin coating unit. Switch on this unit, a message will display which is shown in figure 4. First press “1”to warm up the machine. Warm up process will end automatically in 10 minutes. Then press “2” to load program. A message will display “enter program <1/2>”. Then again Press”1”. Now you can set speed, acceleration and time for spin coating. For this press Edit/Save button. A massage will display “ “Prog-1 set number of steps 1/10”. Than press Edit/Save button once more. Use backspace button, left key and right key to alter the RPM or Time for spin coating. Use the same button to save. Now place your substrate on the stage (chuck) made for rotation. A vacuum pump is connected to the unit. Switch on the pump and press the vacuum button located in spinner. It will suck the sample so that the substrate will not fall down during rotation. Then press “Run” button. A massage will display “press [Run] to start.” Pour the filtered solution on the substrate by the help of a syringe then press “Run” button again. Stage of spinner will start rotating and after set time it will stop. MAKE sure the lid of spin coater should be closed. Spin coating of is done now. Press “vacuum” button to release the vacuum so that we can remove our sample from the stage

1. Spin coat PEDOT:PSS solution as described above with 1200 rpm for 1 min.
2. Annealed PEDOT:PSS coated substrates at 120^{O} C for 10 min on hot plate (Switch on hot plate before staring preparation of PEDOT:PSS solution).
3. After annealing, take out the substrates from hot plate and keep them in petridish. Let the substrates cool before going to active layer deposition.

Figure 4: Spin coating unit.

2 b). Active layer coating and annealing:

4. Take pre-prepared P3HT:PCBM solution .

Preparation of P3HT:PCBM solution:

1. Take 10mg of P3HT and 10mg of PCBM in a round bottomed flask.
2. Add 1 ml of monochlorobenzene to it.
3. Keep magnetic stirrer in that solution.
4. Seal the round bottomed flask with paraffin wax.
5. Keep the round bottomed flask on a magnetic stirrer for good mixing of P3HT:PCBM at room temperature.
6. Solution must be magnetically stirred at least for 6-8 hours.
7. Filter it with a 0.46 micron filter before coating.
8. Spin coating at 1200rpm for 1 minute. Spin coating procedure will be same as above.
9. Anneal at 130°C for about 20 minutes on hot plate and Cool down to room temperature by keeping in a petridish.

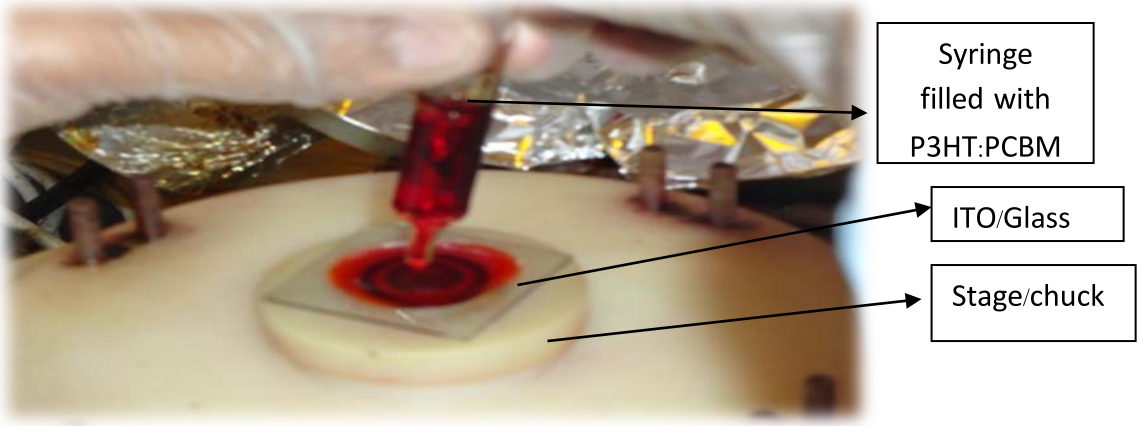


Figure 5: MEHPPV Coating using Spin Coater

3. Cathode deposition

In standard technique Al/Ca is deposited via thermal vapor deposition technique. Here GaIn/Ag paste is used. Use a brush and mask to make cathode as shown in figure.

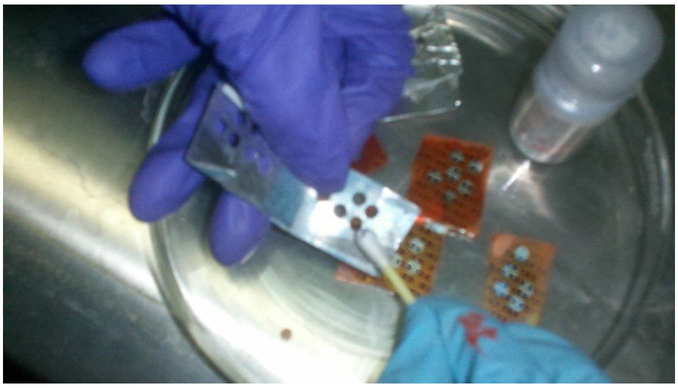


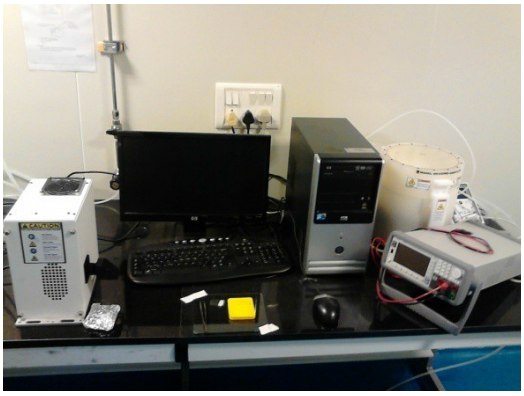
Figure 5: Application of GaIn dots with cotton swab.

4. Characterization:

Calculate efficiency by using solar simulator.

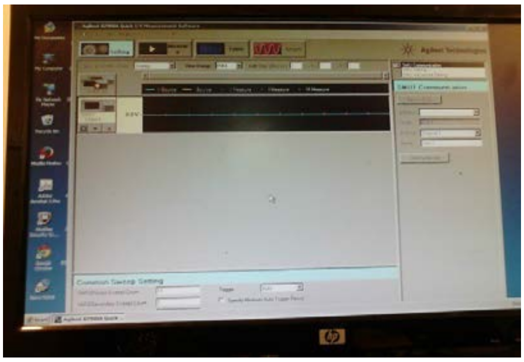
Operation of solar simulator:

Switch on Computer, Agilent B2901A source unit and solar simulator.



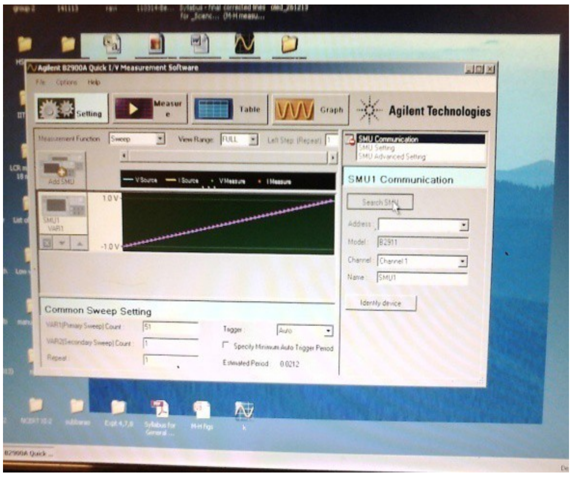
Click on “Start”

Click on “Quick IV measurements software” in the pop up window



Window “Agilent B2901A Quick IV measurements software” appears

Select SMU communication Click on Search SMU



Measurement Function: Sweep

View Range: FULL

Left Step (Repeat): 1

Model: B2911

Channel: Channel 1

Name: SMU1

VAR1(Primary Sweep) Count: 51

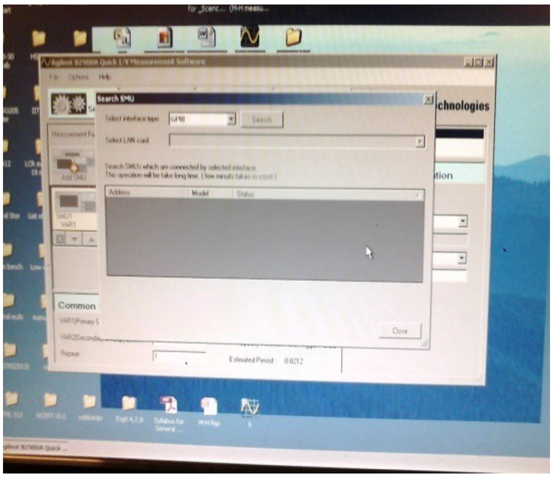
VAR2(Secondary Sweep) Count: 1

Repeat: 1

Trigger: Auto

☐ Specify Minimum Auto Trigger Period

Estimated Period: 0.0212

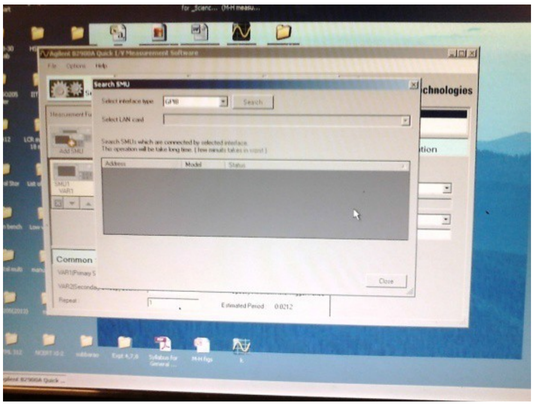


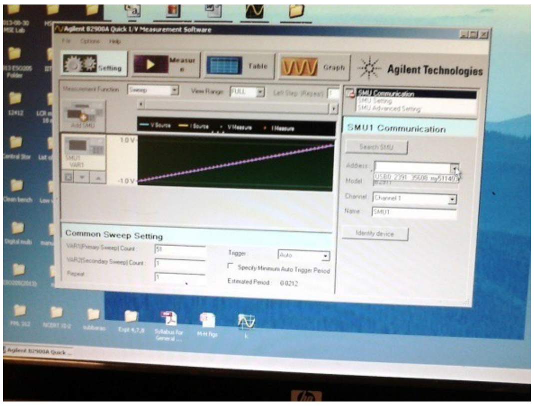
Select interface type: GPIB

Select LAN card

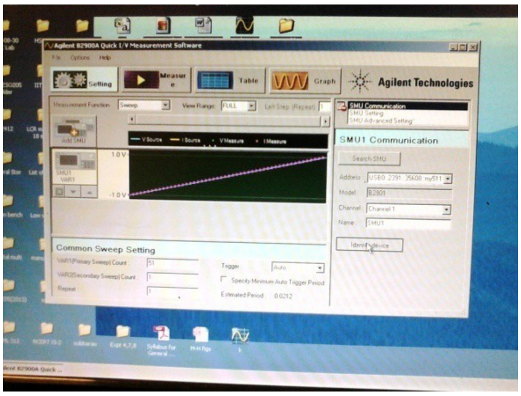
Search SMUs which are connected by selected interface.
The operation will be take long time. (few minuits takes in worst)

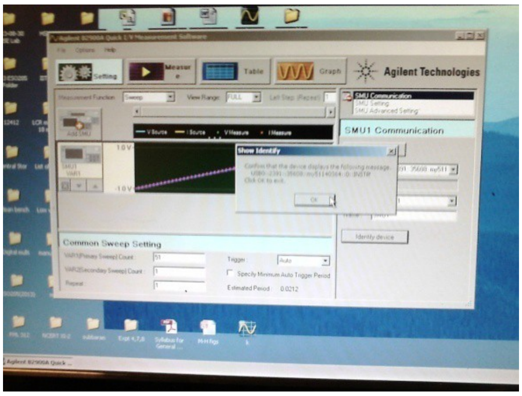
Search SMU window appears



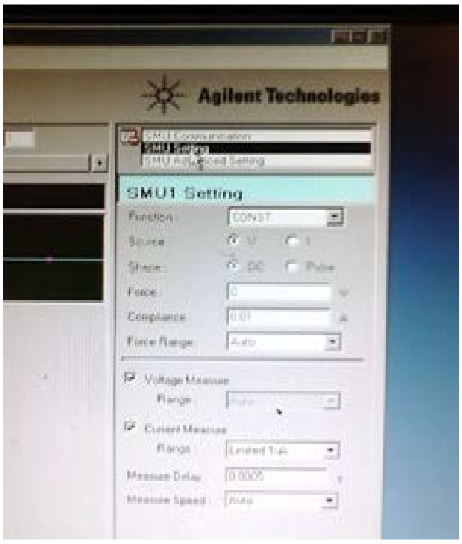


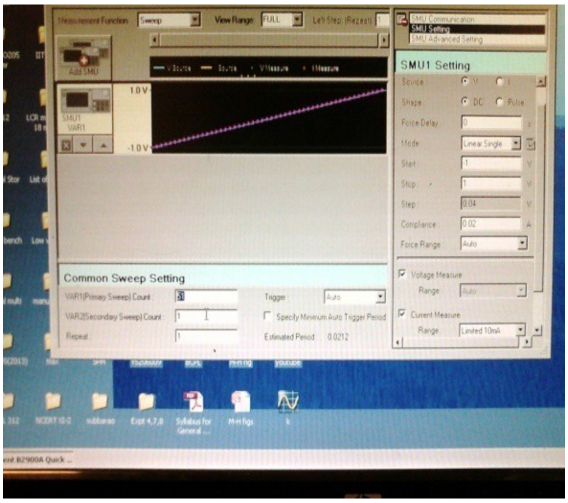
Go to “USB” at Select interface type and “Close”
Click on address and select it
Click on “Identify device”



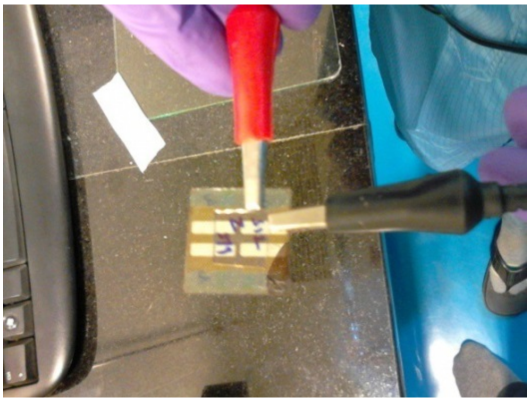


A pop up window “Show Identify” appears, select OK
Go to SMU settings

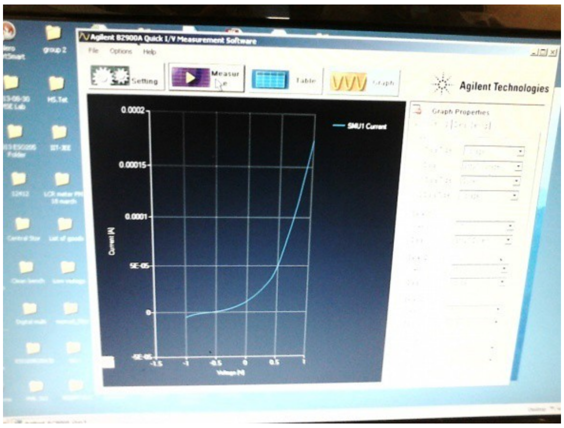




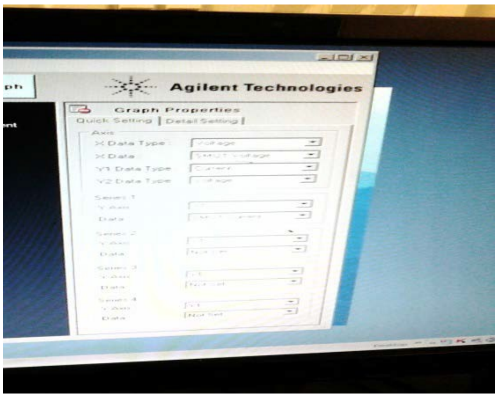
Select Function as “VAR 1” Give appropriate input data
Switching On Solar Simulator:



Turn on Switch of solar simulator simulator before 2-3 min of start of measurement
Take contacts from both Anode and Cathode
Place solar cell facing ITO towards light



Click on “Measure” and select X data Type as “Voltage”



X Data Type: Voltage
X Data: SMU1 Voltage
Y1 Data Type: Current
Y2 Data Type: Voltage

Save the file by using “Save as” option in “qvid” format.

Calculate Voc, Jsc, Fill factor and Efficiency from the IV curve.

Expectations from the Students:

1. Hands-on experience in device processing of an organic solar cell
2. Characterization of solar cells
3. Caclulating V_{OC} and I_{SC}, FF and efficiency.
4. How would you calculate shumt and series resistance? Calcualte these values in your sample?

What should be the ideal value of shunt and series resistance?

EXPERIMENT-9A
Processing of Biomaterials

Aim: To (i) deposit polymer coatings using electrostatic spraying process, and (ii) process bulk structural components using compression molding.

Introduction/ Theory:

In order to fabricate polymeric composites into useful shapes (either as coatings or bulk), it becomes necessary to utilize processing techniques. When a specific surface response is required (such as corrosion resistance, or bio-inertness), it is wise choice to utilize coatings. But, in many cases, a complete polymer composite is required for performing a certain utility (such as making light-weight load-bearing structure, or ability to replace damaged/worn parts). Hence, processing of polymers, both as coatings and bulk structure, is focused in this experiment. In this experiment, students will learn: (i) to utilize electrostatic spraying for developing a uniform polymer coating on substrates, and (ii) compression molding for making bulk polymer composites.

Electrostatic Spraying

Electrostatic spraying (Fig. 9.1) involves inducing an electrostatic charge on the powders, allowing them to repel each other while travelling to the earthed substrate. In this fashion, the electrostatic charge creates mutual repulsion among polymer particles, and disperses them uniformly over the substrate. It is to be noted that electrostatic spraying is only depositing loose powder, so enough care must be taken not to disturb the powder (giving impact or jerk to the substrate) while handling. Now the loose (but uniformly dispersed) polymer can be cured to provide a uniform coating on the substrate.

Fig. 9.1: Electroststatic spray gun showing metal susbtrate for coating.

MethodologyFor Depositing Polymeric Coatings (Using Electrostatic Spraying):

1. Clean and grind the metallic substrate (using 120 and 240 grit papers), which have to be coated.
2. Weigh the sample, and note down the dimensions of the substrate (using screw gauge/ Vernier calipers).
3. Fill the coating powder (of polymer or polymer composite) into the plastic case of electrostatic spray gun.
4. Connect the unit according to labeled diagram as above. Precaution: Do not forget to use the transformer otherwise the fuse will blow off.
5. Connect the earth-wire to the substrate. Use a backing tray so the excess spray powder can be recycled as shown in diagram
6. Connect the spray gun with the adaptor (with transformer from 220V to 110V) which is connected to main source of power supply
7. Switch on the power, trigger to start the fan that will carry the electrostatically charged powder to substrate.
8. Carefully lift the coated substrate. Note that the powder is just mechanically sitting on the substrate. Now, cure the polymer in an oven according to coating powder melting point for a time period (usually for polymers ~ 200 C for 0.5 hr is sufficient for curing.)
9. After curing, weigh the sample, and measure its dimensions.
10. Polish the cross-sectional area to measure the coating thickness using optical microscope.

Compression Moulding:

Compression moulding is a technique principally used for thermoset polymers (Phenol formaldehyde, Urea formaldehyde, Epoxy, Polyester etc.) and some special thermoplastic polymers (Ultra high molecular weight polyethylene). A known weight or volume of the moulding powder is placed in the open mould cavity, mould is closed under pressure, causing the material to flow and completely fill the cavity, pressure being held until the material has cured.

The mould consists of two halves, a male (core) and a female (cavity) part, these mould halves are attached to the upper or lower platen of a press. Heat is applied through the platens. Depending on the characteristics of polymeric material and the design of the mould, the processing temperature ranges from 120°C to 250°C and pressure ranges from 1000 to 10,000 psi (70.5 to 705 kg/cm^2). In general, a molding temperature ~ 10-15 ^{0}C higher than the melting point is required. Therefore, the molding temperature must be higher than the melting point of material.

The mould remains heated and closed until the polymeric material cures and set. The cure time depends on the size and thickness of the product, this cannot be predicted directly, but must be determined by experience or by trial. After the material has cured sufficiently, the mould is opened and the piece is ejected by knockout pins.

Flow properties and variables:

Fluidity is the reciprocal of viscosity, total flow that occurs is the product of flow time and fluidity. Moulding powder material is classified as soft flow or free flow (low molecular weight) and stiff flow or hard flow (high molecular weight). Free flow powder is used in complex mould structure (presence of delicate inserts), but in the other side it may yield more amount of flash in the moulding process. Stiff flow powders often give a better finish and a large flash.

Fine powders give best finished product, but dust problem must be taken care of. In the other hand course powders are less dusty but give a course grained or often orange peel surface. The size of particles is less important if there is a extensive flow of material applied. For palletisation, fine size and moisture free particles are desirable to aid pellet consolidation.

Viscosity of material is the important variable in compression moulding process, which changes with time at certain temperature and pressure. In figure 9.1 the viscosity of the material versus time has shown four stages at stage A- the material is at room temperature and zero pressure. With increasing temperature and pressure, the viscosity decreases as shown along the slope at stage B. Viscosity continues to decrease reaching to a peak at stage C, where acceleration of reaction occurred. Complete curing or reaction cessation at stage D is seen.

The other variables in compression moulding process are also seen which are type and content of material, reinforcement and lubricant.

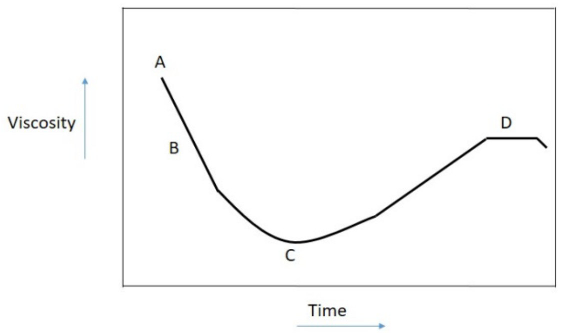


Figure 9.2 Effect of flow variables

Moulding sequence and moulding cycle:

The moulding sequence in compression moulding is as follows in figure 9.3.

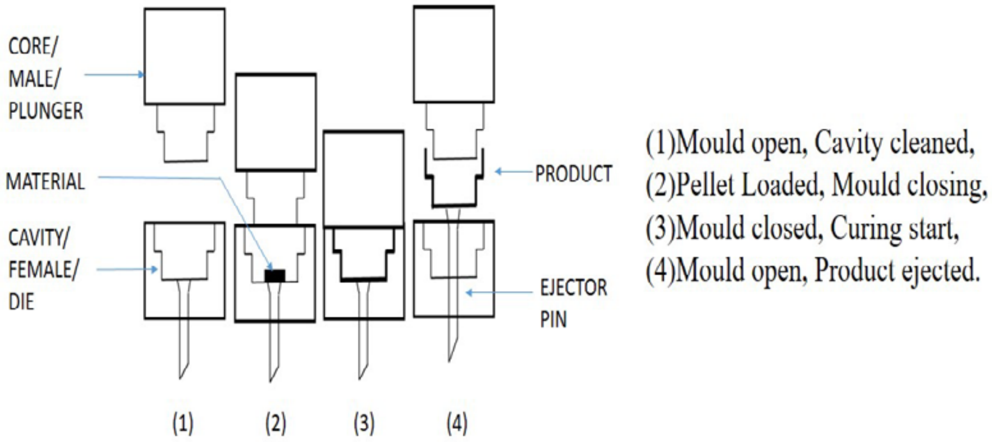


Figure 9.3.Compression moulding sequence

The compression moulding cycle has shown in figure 9.4, where the dwell time has a larger fraction of the moulding cycle.

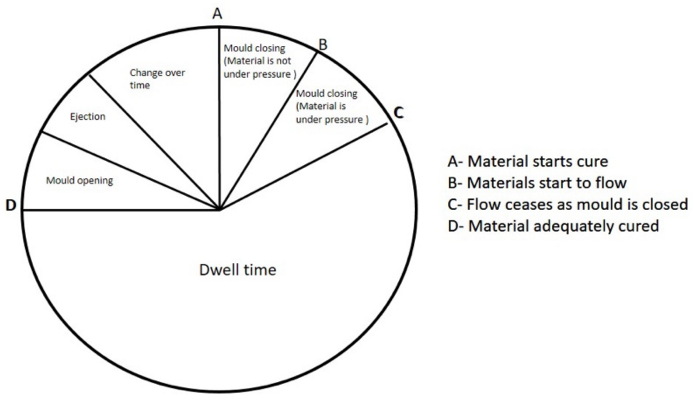


Figure 9.4. Compression moulding cycle

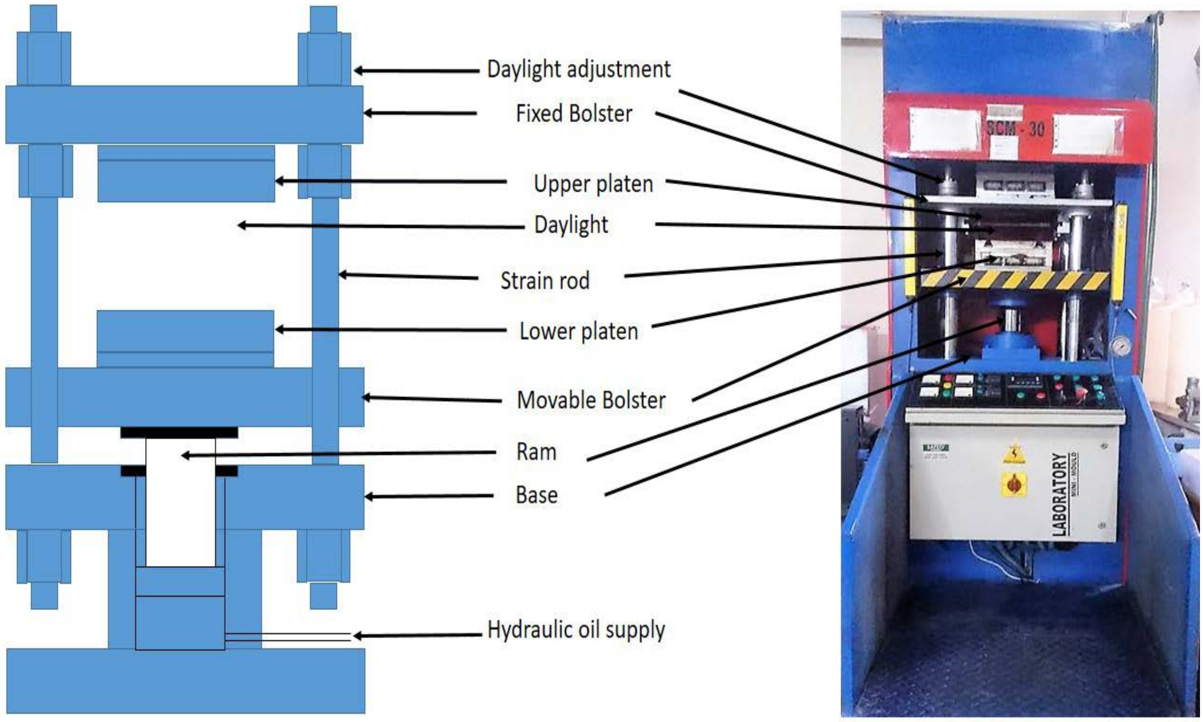


Figure 9.5: Schematic of compression moulding

Compression moulding machine:

The presses used in compression moulding machine are available in many different shapes and designs and can be classified as either hand, mechanical or hydraulic type. The hydraulic type compression moulding machine is explained as below.

Hydraulic compression moulding is again classified as upstroke type and down stroke type. In upstroke type, the hydraulic ram moves the bed of press upward to close the mould. The strain rods or the tie rods hold the upper and lower platen of press in accurate alignment so that the two parts of the mould do not mismatch. Daylight opening is the maximum distance between upper and lower platen, this opening must be large enough for easy handling of mould. The mould is bolted to the upper and lower platen of press. These platens have heating channels, which help to heat the platens when source is applied. During setting up the two platens of the press must be checked for parallelism. In down stroke type, there is a fixed lower bolster and movable upper bolster. It is usually preferred for large size product.

Compression moulds are usually constructed of case-hardened steel, in order to withstand the high pressures of compression moulding. The hydraulic up stroke type compression moulding has shown in figure 9.5

.Advantages, disadvantages and application of compression moulding:

Advantages

- Lowest cost mould,
- Little “throw away “material,

- Lowe labour costs
- Better for large products at lower moulding pressure.

Disadvantages

- Difficulty in ejection of product,
- Accuracy is not achieved.

Applications

- Radio and appliance knobs,
- Sheets for laboratory testing,
- Domestic products.

Methodology For Compression Molding of Polymer Composites:

1. Clean the die and apply silicone oil on the die-surface.
2. Fill the powder in die according to the required thickness of the pellet
3. Set the temperature to 200 C and pressure to 7.5 MPa for compression molding
4. Insert the filled die in between the hot platens (mould)
5. Give the curing time of 40-60 minutes for complete densification
6. Release the pressure and take out the die from the mould and let it cool
7. Now the pellets have to be taken out for testing/characterizations

Expectations from Students:

(i) Measure the thickness of substrate before and after coating, and determine the coating thickness. Also, weigh the substrate before and after and utilize density of material to calculate the coating thickness.

(ii) Polish the coated sample and measure the coating thickness using optical microscopy.

(iii) Use 2-3 variants of polymer composites (a + any of the b/c/ or d):

   a. pure polymer for comparison
   b. additives of 2-5 wt.% alumina (or hydroxyapatite) with varying reinforcing content.
   c. Change the particle size of reinforcements with similar content.
   d. additive of 2-5 wt.% alumina (or hydroxyapatite) AND 2 wt. % carbon nanotubes (CNTs) (provided if CNTS are available).

(iv) Note the weight of starting powders. Compare the weight of compression molded samples.

(v) Note the dimensions of compression molded samples, and calculate the density using weight by volume.

(vi) Observe the densification as the additive contents/ size change.

References:

1. Polymer processing by Baired.
2. Handbook of plastic processing by J.A Brydson.

EXPERIMENT - 9B

Effect of Surface Modification on Bacteria/ Cell growth

Aim: To learn the effect of surface modification on bacteria/ cell growth (two demonstrations).

Introduction/ Theory:

"Any substance or combination of substances, other than drugs, synthetic or natural in origin, which can be used for any period of time, which augments or replaces partially or totally any tissue, organ or function of the body, in order to maintain or improve the quality of life of the individual is called Biomaterial" (American National Institute of Health). Biomaterials can be broadly defined as synthetic materials, which have been designed to induce a specific biological activity, i.e. to remain in a biological environment without damaging the surroundings and without getting damaged in that process. The materials for implantation are selected on the basis of various properties and are typically metals and alloys, ceramics or polymers along with their composites. Appropriate biological response of a material in physiological environment far exceeds the mechanical and tribological response of material without affecting the normal body functions. Thus, the prime aspect of a biomaterial is that how it interacts with cells and tissues when it is implanted *in vivo*.

Biomaterials can be classified into three main categories on the basis of various types of host responses after their implantation into the living body.

a) **Bioinert / biotolerant:** Bioinert materials are biocompatible materials, but those can not induce any interfacial biological bond between implants and bone.
b) **Bioactive:** Bioactive materials are a group of biocompatible materials, which can attach directly with body tissues and form chemical/biological bond during early stages of post implantation period.
c) **Bioresorbable:**Bioresorable materials are the type of biocompatible materials which is gradually resorbed and finally disappears and is totally replaced by new tissues, *in vivo*.

In vitro tests are lab scale simulated experiments, which are required as first step of initial screening. It must be noted *in vitro* tests do not provide inflammation or immune response, and utilize only single cell-lines, thus, obviating complexity that might arise out of actual tissue environment *in vivo*. Though *in vitro* tests may not be completely representativeof actual physiological environment, nevertheless, these serve as effective first step in evaluating biocompatibility of biomaterials.

On the front of bacterial infection, the genesis of failure of medical implants is mainly attributed to bacterial biofilm build up. Biofilm consist of a community of microorganisms (such as bacteria, fungi, yeast, etc) held together by a matrix, in which the microorganisms cooperate and interact with one another. Biofilm incorporates clusters of microorganisms (called as *colony*) are located thoruughout the matrix, and may contain only one organism or a variety of different microorganisms. Microcolonies provide channels for the transport of oxygen, nutrients, waste, and other particles. Many a times, microscale layers within a biofilm contain cells of the same species exhibit dissimilar phenotypes that results in variation of oxygen concentration gradients, pH differences, and other environmental effects.

Bacteria are unicellular prokaryotic microorganisms (no membrane bound organelles) or simple associations of similar cells ranging few micrometers in length and have shapes ranging from spheres to rods and spirals. Bacterial cell is surrounded by a lipid membrane, or cell membrane, which encloses the contents of the cell and acts as a barrier to hold nutrients, proteins and other essential components of the cytoplasm within the cell. Bacteria lack a nucleus, mitochondria, chloroplasts and the other organelles present in eukaryotic cells (such as the Golgi apparatus and endoplasmic reticulum). Bacteria do not have a membrane-bound nucleus, and the nucleoid contains the chromosome with associated proteins and RNA. Flagella are rigid protein structures, about 20 nanometers in diameter and up to 20 micrometres in length are used for motility. Bacterial adhesion can be described as physicochemical interactions (balance of attractive and repulsive interactions) by which bacteria adhere firmly to a material substrate or biological cell/tissues. Bacterial adhesion and subsequent cell growth on a surface have important roles in a variety of systems including biomaterial development and bacterial delivery systems used for bioremediation.

Cell-Culture Methodology:

Primary cell culture

Apparatus: 70% (V/V) ethanol, medium (here DMEM supplemented with 10% FBS and 1% antibiotic), Water bath, CO_2 incubator, T-25 flasks, Cell stock, Sterile pipettes and steripipette

Note: The process of cell culture is performed in a L.A.F (Laminar Air Flow) hood and anything which is to be introduced into the hood is washed thoroughly with 70% ethanol.

The process for culturing L929 (mouse fibroblast cell line).

1. Take out 5 ml of DMEM media using pipette into a T-25 flask.

2. The frozen cells in cryovial stored in the liquid Nitrogen, as stock, are taken out and thawed in water-bath at a temperature of 37 ˚C.
3. This thawed cell suspension is pipetted out into the T-25 flask containing 5 ml DMEM media.
4. This flask is now kept into a CO_2 incubator for a period of 2 days.

Sub-culture of cells

Requirements: Primary culture of cells, Autoclaved and Filtered IX PBS, Trypsin-EDTA, Medium (here DMEM supplemented with 10% FBS and 1% antibiotic), Water bath, CO_2 incubator, T-25 flasks, Sterile pipettes and steripipette, 70% (V/V) ethanol

Procedure of sub-culture involves the trypsinization of the cells and is as follows-

1. Frozen Trypsin-EDTA, IX PBS and DMEM media is taken out from 4˚C and brought to room temperature keeping in 37 ˚C water bath for until normal.
2. The primary culture i.e. the T-Flask containing the cells is taken out from the incubator and the media present in it is discarded.
3. It is then washed by up and down pipetting with IX PBS.
4. 1 ml of Trypsin-EDTA is added to this and this is left for approximately 1-2 minutes until all the cells detach from the surface.
5. Approximately 1.5 ml of Media is added to this to neutralize the effect of Trypsin.
6. The cell suspension is pipetted out equally into 2 small centrifuge tubes (eppendorf) and further centrifuged for 1-2 minutes.
7. In the meantime media is added to 2 T-25 flasks.
8. The collected supernatant is discarded and the pellet in the eppendorf is redissovled by adding 1 ml media to each of the two eppendorf tubes.
9. This dissolved cell suspension is then pipetted out equally into the two T-flasks containing fresh media.

Seeding

Requirements: Sub-culture of cells, Autoclaved and Filtered IX PBS, Trypsin-EDTA, Medium (here DMEM supplemented with 10% FBS and 1% antibiotic), Water bath, CO_2 incubator, T-25 flasks, Sterile pipettes and steripipette, 70% (V/V) ethanol (See Fig. 12.1)
The cultured cells are now ready to be seeded onto our samples. This process includes the following steps

1. The specimen and a control sample (normally a coverslip also) is cleaned and sterilized and kept into a well plate, followed by its further sterilization with ethanol and UV.
2. Trypsinization is performed on the cultured cells as mentioned in the previous process

until step 8. This is performed for each of the two T-Flasks separately.

3. After reaching the step 8, 10µl of the cell suspension is pipetted out and loaded onto a haemocytometer (its counting squares covered with a coverslip) by holding the tip of a pipette filled with suspension and allowing it to fall dropwise. This suspension is drawn under the coverslip by the capillary action. This is performed inorder to count the number of cells
4. Allow the cells to settle on the haemocytometer and observe in under the microscope and count the cells in 5 squares(1 in the middle and 4 at the corners separated by triple lines)
5. Cells per mL is determined by the following calculations: Cells/ml = average count per square $\times 10^4$
6. The formula $C_1V_1 = C_2V_2$ is used to calculate the volume of the cells needed to seed onto the sample, where C_1 is the calculated cells/ml, V_1 is the volume of cells to be taken from the supernatant obtained in step 2, C_2 is the total concentration of the cells which is optimized by practice and V_2 is the total volume of the cell suspension required for seeding on the samples.From this V_2 volume, 1 ml is pipetted out into each well of the well plate containing the sample.
7. This is then kept in the CO_2 incubator for a period of 2 days.
8. With the remaining cell suspension the same process is repeated and the cells are divided equally into T-flasks containing media and incubated further.

12.1.2.3: Drying:

1. After the completion of 48 hrs, the cells are further fixed with 2% (V/V) gluteraldehyde by adding 700µl into each well containing the sample.
2. This is washed with PBS and then serially dipped into various dilutions of ethnol as 30, 50, 70, 95 and 100% (V/V).
3. Hexa Methyl Di-Silane is used as a critical point dryer to dry the sample completely.
4. Now the sample is ready to be gold coated and further observed under Scanning Electron Microscope.

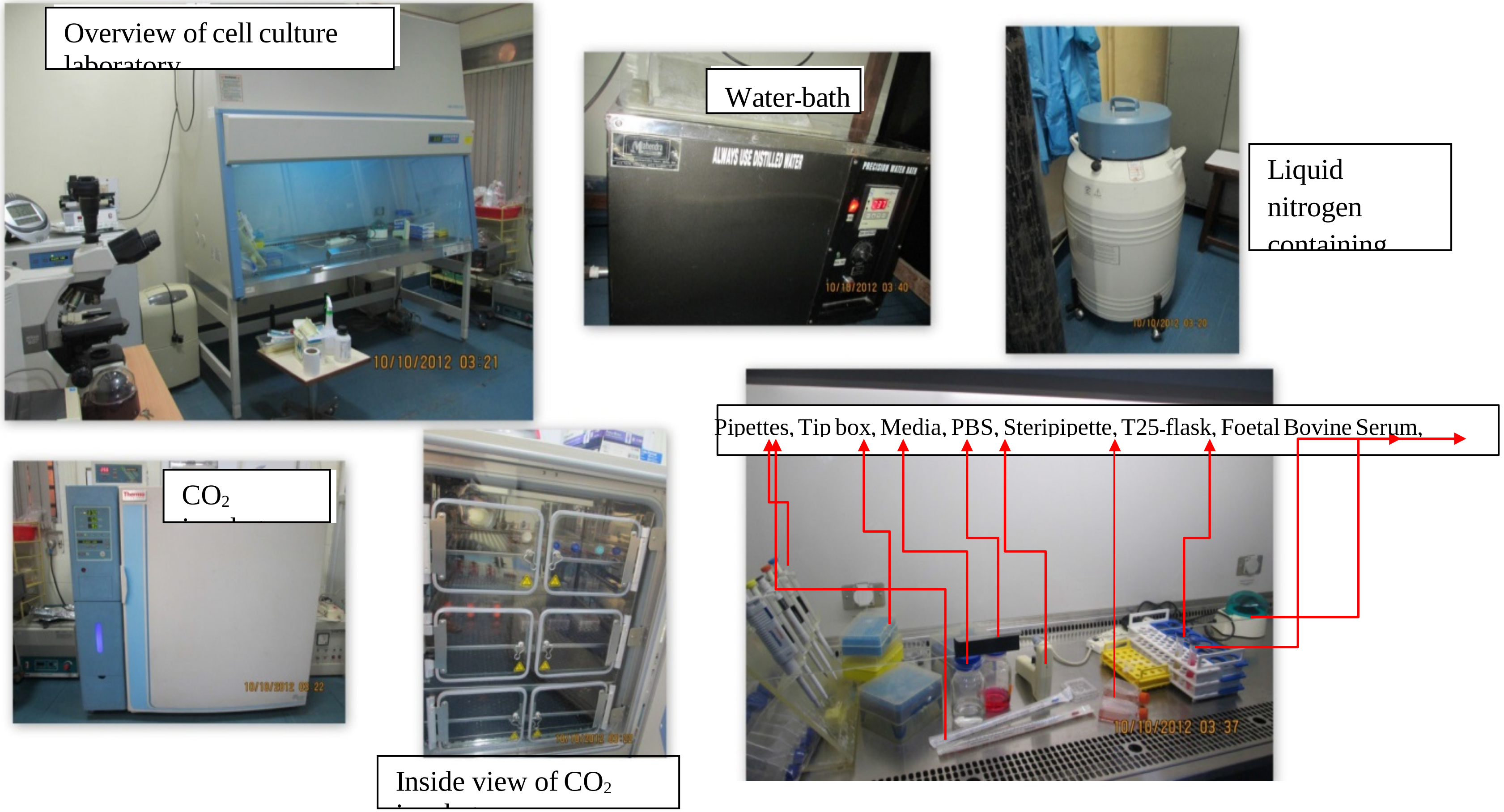


Fig. 12.1: Images of apparatus used in cell-culture.

Bacteria Culture Protocol

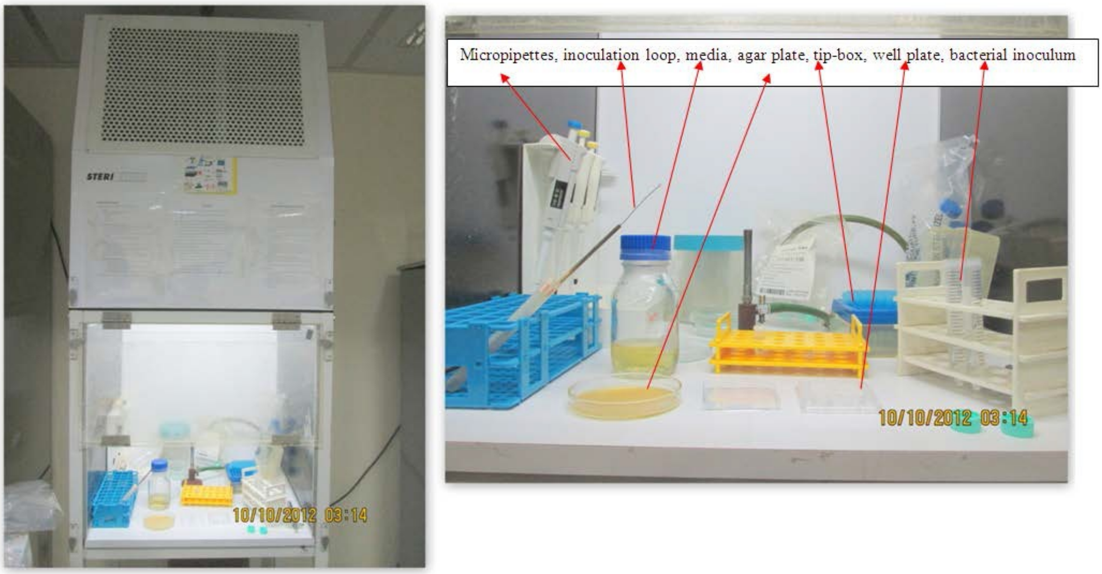
Apparatus: Bacterial inoculums, Autoclaved and Filtered IX PBS, Required medium, CO_2 incubator, Agar plates, Sterile pipettes and micropipette, 70% (V/V) ethanol (See Fig. 12.2)

Methodology:

1. Samples to be tested are first cleaned and sterilized according to need.
2. These samples are kept into a well plate and further washed with ethanol, followed by PBS and UV sterilization.
3. 1 ml of bacterial suspension is taken in eppendorf and centrifuged at 2000 rpm for 5 minutes. Supernatant is discarded and pellet is re-suspended with fresh Luria Broth (LB) media and vortexed.
4. 100µl of this suspension is used for seeding of each sample.
5. Equal volume 500 µl of LBis added to each sample.
6. This is incubated for 4hrs at 37^0C.
7. Samples are then washed (rinsed) twice by 1X PBS and then soaked in primary fixative 3% gluteraldehyde for 20 minutes and further in)0.1M Sodium Cacodylate for 15 minutes.
8. Samples are then again washed with 1X PBS.
9. The cells onto the samples are dehydrated by washing the samples and dipping it in serial dilutions of ethanol as 30, 50, 70, 95 and 100% for 10 minutes each twice.
10. Critical point dryer Hexa Methyl Di-Silane is used to dry the sample completely.
11. Dried samples are sputter coated with gold and observed under SEM.

Expectations from Students:

- i. Learn the protocol for culturing the bacteria
- ii. Observe the effect of surface modification on cell viability
- iii. Role of antibacterial agents in eliciting bactericidal property.



Overview of bacteria culture laboratory

Fig. 12.2: Image showing the apparatus required for bacteria culture.

EXPERIMENT-10

Tribology of Biomaterials

Aim: To evaluate tribological performance of: (i) biomaterial with modifier (ii) biomaterial without modifier, and comparing their relative wear performance

Introduction/ Theory:

Tribology comprises of wear, lubrication and friction among mating surfaces. There can be various parameters incorporated in quantifying the tribological response, which can be: wear loss (in terms of weight or volume), friction coefficient, mechanism of wear, friction hysteresis, etc. Wear is the removal of material from body surfaces in contact or relative motion due to interaction with each other. Friction can be defined as the resistance to relative motion of bodies in contact. It is to be noted that when an implant is inserted *in vivo* (inside body), then the mating surfaces may abrade the adjoining surfaces and release wear-debris in body. In order to process a material, various modifiers may also be added during fabrication of usable parts, which may apparently alter the material response when in use. Thus, it becomes critical to evaluate the tribological response (wear weight/volume) and compare the wear performance of various implant materials.

Tribological test is performed using an abrading pin or ball (made up ceramic or metallic material) against the material to be tested using a tribometer (Fig. 10.1). Adhesive or abrasive wear can dominate depending on the type of material adjoining each other. Ceramic to ceramic will result abrasive wear, whereas metal to metal contact will result mostly in adhesive wear. Whereas, in case of polymers, the abrading pin might just displace the material, thus, the loss of dimensionality through wear volume might be a better representation of wear-damage. Nonetheless, weight-loss will be evaluated in the current experiment, and then using the density of composite, a corresponding wear volume can be calculated. If available, surface topography using profiling technique can also be utilized in order to evaluate exact wear volume.

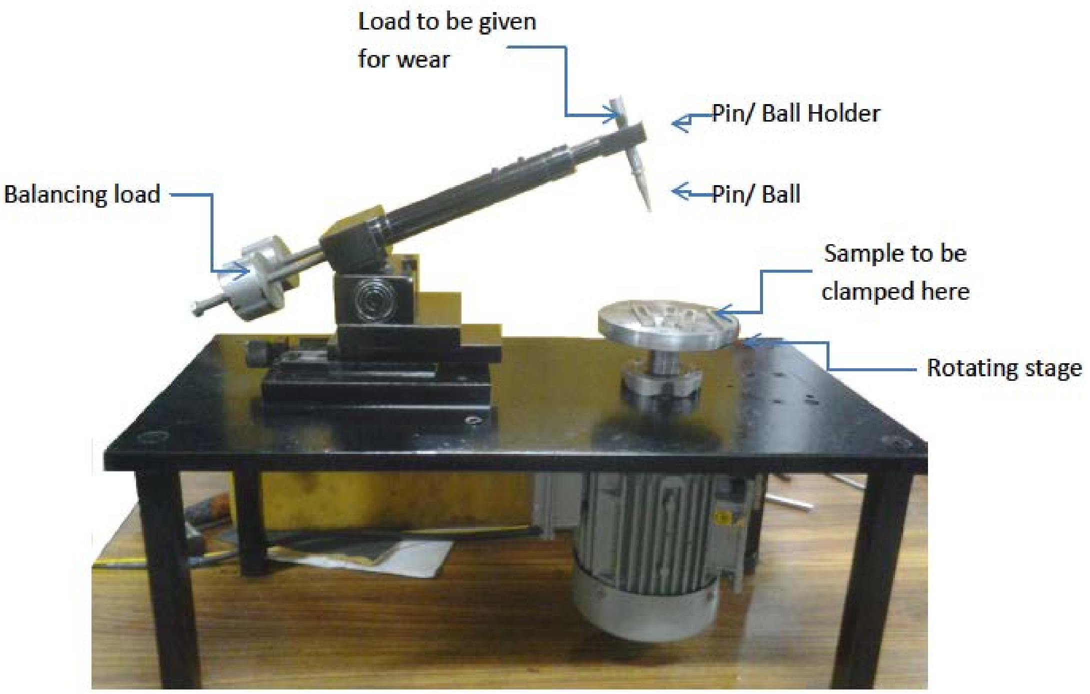


Fig. 10.1: Image of a Tribometer.

It will be interesting to see the way the coefficient of friction changes during the initial period (called running-in period). Coefficient of friction is not being measured in this experiment. You may also appreciate the role of loading conditions, or time in affecting the wear volume.

Methodology:

1. Select the abrading pin/ball you want to use (mostly steel ball).
2. Balance the cantilever-arm of the tribometer using set-screws so that no load is imparted on the sample.
3. Raise the tribometer arm and set friction to zero by clicking “0” button.
4. Clamp the sample on platform/chamber
5. Put the lubrication hose in the chamber if required.
6. Lower the arm and put the rubber ring on the pin/ball Load the required weight on the pin/ball using the available top-slots over the load section.
7. Adjust the height of the profiler over weight such that intensity of 60-80 or above and depth up to 50-60% are indicated.
8. Check if lubrication is required.
9. After making necessary adjustments, lower the arm and start the test.

10. Weight the sample weight: (i) after decided number of cycles, and (ii) after the test is over.
11. Test will start according to the set parameters.

Calculation of Wear Damage:

The surface profiles of worn surfaces were obtained by laser surface profilometer (LSP) (Perthometer PGK 120, Mahr, Germany) using an infra-red laser beam of wavelength λ= 780 nm. The profilometer scans the sample line wise and cross sectional area of wear track can be found to get the volume of wear valley.

$$\text{Wear volume}(V) = \text{area of cross section of worn valley} \times 2\pi R = A \times 2\pi R \qquad (1)$$

where R is the radius of wear track.

The wear constant is defined as,

$$\text{wear constant } (k) = \frac{\text{wear rate } (W) \times \text{hardness}(H)}{\text{load } (P)} \qquad (2)$$

The wear volume can also be obtained by optical microscopy or by measuring weight loss before and after wearing, which can be converted to wear rate as below:

The wear rate is given by:

$$\text{wear rate } (W) = \frac{\text{wear volume } (V)}{\text{load } (P) \times \text{sliding distance}(l)} \qquad (3)$$

<u>Expectations from Students:</u>

i) Role of hard abrasive coating on the wear resistance of material (with respect to number of cycles or change in load). Take readings every 5,000 cycles and measure the weight loss.

ii) Appreciate the coefficient of friction between different surfaces
   a) Metal and polymer: Use metallic ball and polymeric substrate for finding the wear between metal and polymeric mating surfaces.
   b) Ceramic and polymer: Use ceramic pin and polymeric substrate for finding the wear between ceramic and polymeric mating surfaces.

iii) Wear damage in terms of the Penetration depth (in-situ): Take readings every 5,000 cycles and measure average depth from depth-sensor. Assuming the geometry (from optical microscopy), also calculate equivalent wear volume.

EXPERIMENT-11

Biomimetics/ Surface modification

Aim: To (i) measure contact angle of various surfaces, (ii) learn the effect of surface energy on wetting of surfaces, and (iii) finding role of surface roughness/ chemistry on affecting the wettability of surface.

Introduction/ Theory:

Tribology term is derived from the Greek words: tribo (to rub) and logia (logy: study of or knowledge of). Polymers such as ultrahigh molecular weight polyethylene or Teflon have low surface energy, whereas metal surfaces possess high surface energy and are negatively charged. On the other hand, polymeric surfaces are less electrostatically charged and hydrophobic. Generally, hydrophilic materials are more resistant to bacterial adhesion than hydrophobic materials.

The surface energy of solid surface (σ_s) can be calculated with the help of contact angle (θ) as shown in Fig. 11.1 using equation (1):

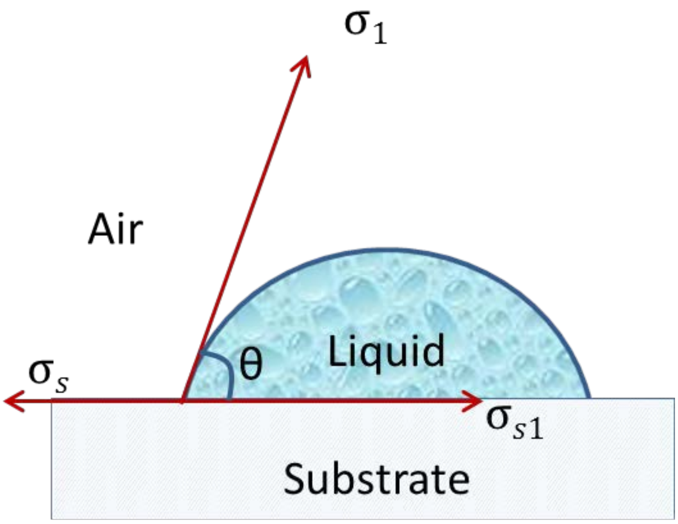


Fig. 11.1: A droplet making a contact angle θ with the solid surface.

$$\sigma_s = \sigma_{s1} + \sigma_1 . \cos\theta \qquad \textbf{(1)}$$

σ_{s1} = Interfacial tension between drop and solid
σ_1 = surface tension of liquid

This contact angle can be measured using a camera, or can be analyzed through more sophisticated optical contact angle measurement unit (Fig. 11.2) which utilizes various models in taking care of the curvature and self-sagging effects of liquid droplet.

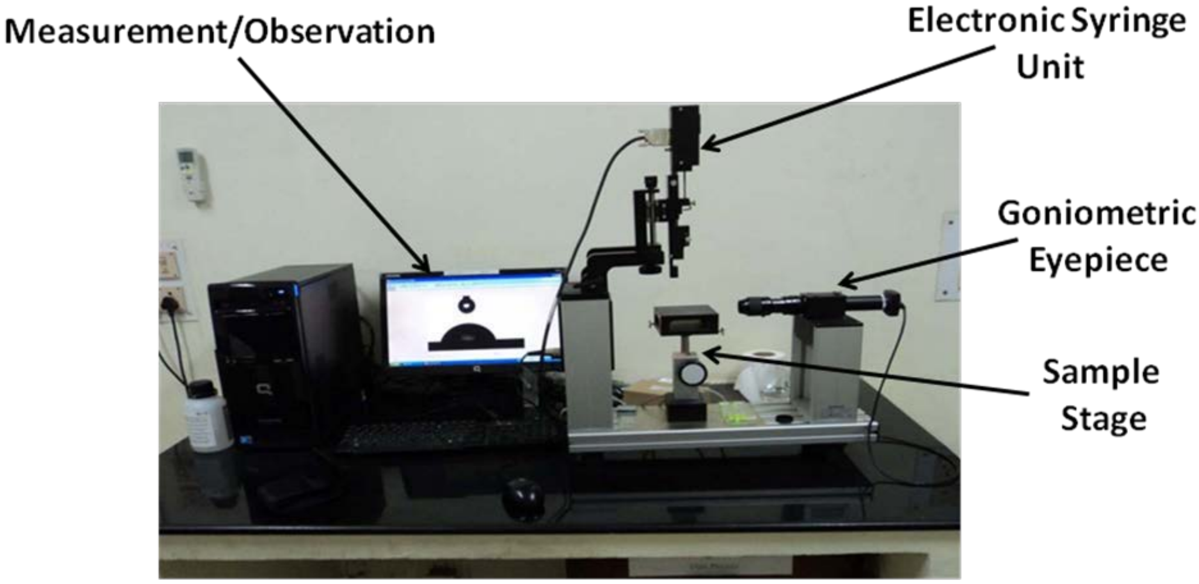


Figure 11.2.: Set-up for contact angle measurement

Usually, water and n-hexane were used for contact angle measurement to calculate the surface energy. Further, the polar and dispersion parts of surface free energy can be calculated by the Owens–Wendt–Rabel–Kaelble geometric mean equations as given below:

$$\sigma_1 = \sigma_1^d + \sigma_1^p \qquad (2)$$

$$\sigma_s = \sigma_s^d + \sigma_s^p \qquad (3)$$

$$\sigma_{s1} = \sigma_s + \sigma_1 - 2\left(\sqrt{\sigma_s^d . \sigma_1^d} + \sqrt{\sigma_s^p . \sigma_1^p}\right) \qquad (4)$$

$$\frac{1 + \cos\theta}{2} . \frac{\sigma_1}{\sqrt{\sigma_1^d}} = \sqrt{\sigma_s^p}\sqrt{\frac{\sigma_1^p}{\sigma_1^d}} + \sqrt{\sigma_s^d} \qquad (5)$$

Where,

σ_s^d & σ_s^p = Dispersion and polar components of solid respectively

θ = Obtained from the CA measurements

Surface free energy:

Take a piece of a material and try to divide it into two parts. To accomplish this task, some energy needs to be spent in order to overcome interatomic forces holding the parts together. If the separation of the parts is carried out so gently that no deformation is induced in the bulk material, the energy spent can be associated with the excess energy of the two new interfaces formed. In theory, assuming that the above action can be reverted, the same amount of energy should be regained upon putting the two parts back together.

In real systems, the splitting up a material into smaller parts always induces stresses and deformations in each of the parts formed, and therefore some energy is dissipated as heat and some is stored as elastic deformation. As a consequence, the accurate experimental determination of surface energy is only possible for isotropic liquids, in which bulk stresses quickly relax and the excess surface energy coincides with the surface tension. For solids, the true value of the surface energy cannot be measured. When applied to solids, the term "surface energy" acquires a totally different meaning and can be viewed as an "adhesive" parameter characterizing the affinity of the surface to other materials. The higher the surface energy of a solid, the more energy is gained upon bringing this surface into contact with other materials.

Interfacial interactions play a key role in all multicomponent materials irrespectively of the number and type of their components or their actual structure. Recognition of the role of the main factors influencing interfacial adhesion and proper surface modification may lead to significant progress in many fields of research and development, as well as in related technologies [1].

Why measure surface free energy?

Ability to measure the surface energy of various materials is essential for ensuring compatibility between the given base material and the top coating one wishes to apply onto it or other materials one wishes to attach to it. The most straight-forward applications include matching a paint to a substrate or matching an adhesive formulation to the materials one expects to be glued together.

In many industrial applications, special tools are used for modifying the surface energy of various materials at will. Thus, to promote adhesion, the surface can be "activated" by plasma treatment or chemical etching, whereby its energy is increased, or on the contrary, it can be passivated by lubrication, silylation, or hydrogenation (see Figure 11.3). For instance, to ensure good adhesion of printing ink to polyethylene or plastic film, such as used in the production of packaging bags, the surface of the film is plasma-treated prior to printing. The same method can be used to enhance the adhesion of the polyethylene-polypropylene laminate applied to the surface of paperboard, which is an essential operation in the paperboard converting technology, or the adhesion and endurance of a teflon layer on the surface of kitchen items. Dewaxing a metallic surface is needed prior to lacquering to ensure good adhesion of lacquer to metal. Waxing a car does not only adds glance but also reduces the adhesion of dirt to the lacquer. And after teflon-based waxes have become available on the market, care needs to be taken that a paraffin-based wax not be applied over a teflon- based one, while doing it the other way around would work fine.

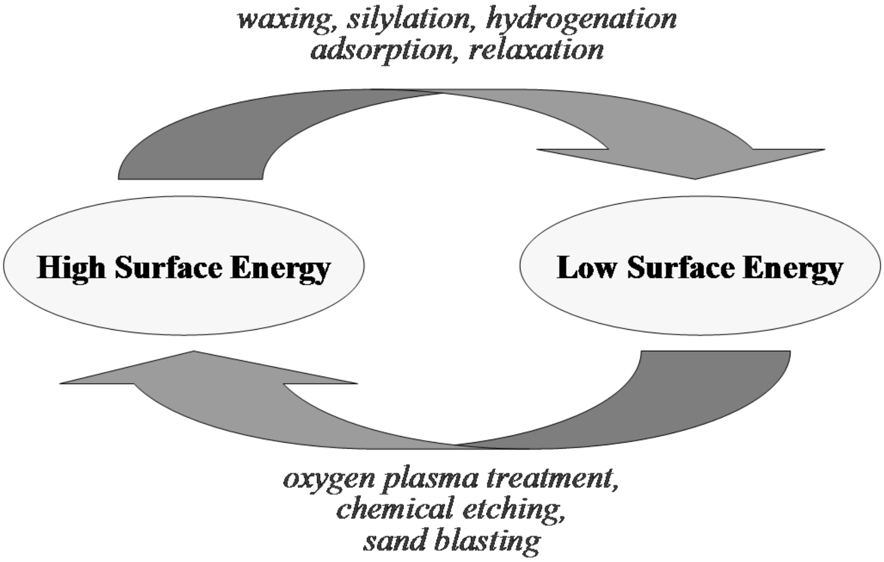


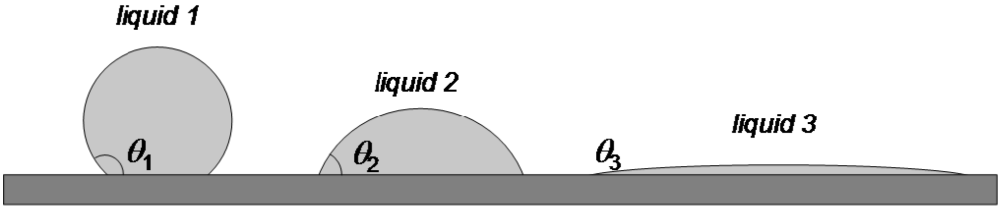
Fig.11.3: Common industrial processes for tuning the surface energy of materials to application needs

This line of examples can be easily extended: adhesion between oil and soil in oil recovery applications, between a surgical implant and a body tissue in medical and dentistry applications, between ink and printed substrate in printing, between fountain solution and fountain roller in flexography, between lubricant and hard coatings in metal-working applications, between cleansing tissue and cleansing liquids used for makeup removal, between hairspray and hair, between absorbents and body fluids, between nail varnish and nails, etc. Obviously, in such applications, the extent of the pre-treatment needs to be optimized and controlled on-line for achieving the best result.

A. Determination of the critical surface energy

The critical surface energy, also known as the critical surface tension, characterizes wettability of the material surface by various liquids. Solids possessing a high critical surface energy are wettable by most liquids, while solids possessing a low critical surface energy are not wettable by most liquids and special means are to be deployed to promote wetting.

The standard determination procedure is outlined in Figure 11.4. A flat and smooth surface of the material in study is prepared and thoroughly cleaned from possible contamination. Then the contact angle values are determined for a number of liquids (one may chose anything from liquid fluorocarbons having extremely low surface tension, 15 mN/m, to mercury, having a very high surface tension of 470 mN/m). The measurement procedure is extremely simple: a small liquid drop is deposited onto the surface and the contact angle is determined from the digital image of the sessile drop, or, for small contact angles below 10^o, from the drop spreading diameter. The appropriate liquid drop size for such measurements is 0.1 ml. A Zisman plot – type graph is made where the surface tension of the test liquids is plotted on the X-axis, and the cosine of the corresponding contact angle on the Y-axis. The extrapolation of the $\cos\theta$vs γ curve to $\cos\theta = 1$ (corresponding to the zero contact angle, or the complete wetting limit) gives the value of the critical surface energy of the material tested. Some examples are included in the Table in Figure 11.4



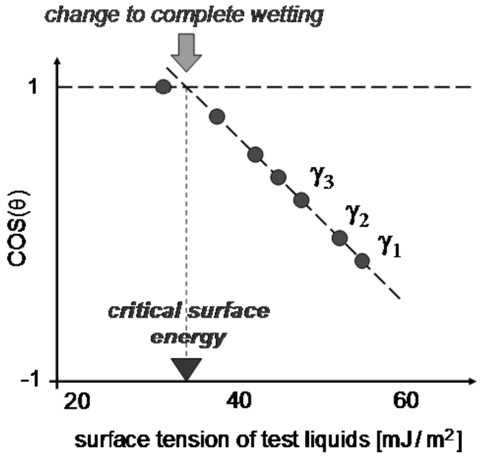


TABLE 1 Critical surface energy of some polymeric materials

Substance	C.S.E. [mJ/m^2]
Teflon	17
Polyethylene	31
Cellulose	40
Urea-formaldehyde resin	60

Fig.11.4: Determination of the critical surface energy of solids

It should be pointed out that the critical surface energy is not really surface energy in a traditional sense; it is rather a wettability benchmark. The critical surface energy shows the maximum surface tension a liquid may have to ensure complete wetting of a given material. In other words, any liquid having a surface tension below the critical surface energy of a given surface will wet that surface completely, forming a uniform surface film. Such behavior is desirable for paints, lacquers, varnishes, lubricants, etc.

B. Partitioning surface tension into dispersive and polar components

Let's demonstrate how to determine the polar and the non-polar dispersive components of the surface energy of a solid based on the contact angle measurements for two different liquids. We will choose the Fowkes equation as our equation of state. In this case, the adhesion energy is a sum of two partial contributions, each of which is expressed as the geometric mean of two adhesion parameters, γ_L and γ_S, the first of which characterizes the "adhesive power" of the liquid, and the second, of the solid,

$$\gamma_L(1+\cos\theta) = 2[\sqrt{\gamma_L^d\gamma_S^d} + \sqrt{\gamma_L^p\gamma_S^p}\,]$$

The adhesion parameters of some common test liquids are known (see Table 2). Therefore, by measuring the contact angles for two different liquids, the remaining two parameters - those of the solid in study - can be found.

TABLE 2 Adhesion parameters for some test liquids

Test Liquid	γ_L (mJ/m^2)	γ_L^d, (mJ/m^2)	γ_L^p, (mJ/m^2)
Water	72.8	21.8	51.0
Ethylene glycol	48.0	29.0	19.0
Diiodomethane	50.8	50.8	0.0

Let's assume that, for the material the surface energy of which we want to determine, the contact angles with water and diiodomethane were found to be 49.6° and 75.2°, respectively. In this case, the following algebraic system of equations needs to be solved,

$$\mathbf{72.8 \times (1 + \cos 49.6^o) = 2[\sqrt{21.8 \times \gamma_s^d} + \sqrt{51 \times \gamma_s^p}]}$$

$$\mathbf{50.8 \times (1 + \cos 75.2^o) = 2[\sqrt{50.8 \times \gamma_s^d}]}$$

whence we get $\gamma_s^d = 20$ and $\gamma_s^p = 30$ mJ/m^2

Hence, surface energy of the solid, $\gamma_S = 20+30 = 50$ mJ/m^2.

Eventually, the polar part can be further sub-divided into acid and base parts, in which case one gets [2],

$$\gamma_L(1+\cos\theta) = 2[\sqrt{\gamma_L^d\gamma_S^d} + \sqrt{\gamma_L^{acid}\gamma_S^{base}} + \sqrt{\gamma_L^{base}\gamma_S^{acid}}\,]$$

The physical meaning of the acid and base adhesion parameters is rather vague, though

Methodology:

1. Place the sample on the stage or into the temperature controlled chamber .
2. Fill the test liquid in the syringe and insert into the syringe unit.
3. Position the sample and the dosing needle.
4. Adjust the magnification and lift the stage up until the surface of the sample is visible.
5. Get the needle in the middle of the image.
6. Adjust the desired distance between needle and sample surface .
7. Dispense the liquid on the sample.
8. Capture the drop image.
9. To determine the contact angle read the angle between the base line and the cursor line in the eyepiece.
10. Click on the options -Magnification → Profile extraction→ Calculate Angle.

- **Calculation of Contact Angle or Surface Tension-** The contact angle (SessileDrop method) or the surface tension (Pendant Drop Method) is calculated according to theYoung- Laplace equation.
- **Calculation of the Surface Free Energy of Solids**-

- Select the liquids (any three will be provided (among Propanol, Xylene, EthyleneGlycol, Diiodomethane Formaldehyde, n-Hexane, Glycerol) whose contact angle with the substrate have been measured) in the combo-box liquid or type the surface tension and their components (if not available in the liquid database).
- Now enter the measured contact angle manually.
- The choice of liquids depends on the selected analysis method (Zisman,Fowkes,Acid-base theory etc). Enter enough (but not more than 4) liquids and click on the Calculate-button to calculate the surface free energy and get the corresponding graph.

<u>Expectations from Students:</u>

i) The role of surface energy on wetting. Surface energy has to be calculated on at least three surfaces.

ii) To render various degree of surface roughness to one of the substrates (by grinding it on emery paper), and see the change in contact angle.

iii) Role of surface chemistry and roughness on wettability. Select one emery paper, and roughen all the samples and measure the change in the contact angle.

References:

1. B. Pukánszky, Eur. Polymer J. 41 (2005) 645.

2. R.J. Good and C.J. van Oss, "The Modern Theory of Contact Angles and the Hydrogen Bond Components of Surface Energies" in "Modern Approaches to Wettability" (M.E. Schrader and G.I. Loeb, Eds.), Plenum, New York, 1992, p.1

EXPERIMENT No.-12

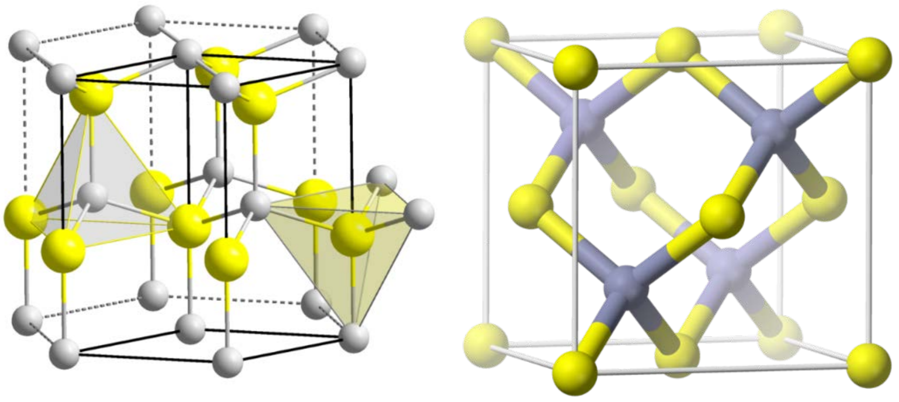
Characterization of Zinc Oxide Semiconductor

Objective: Characterization of Zinc Oxide thin film semiconductor using UV-Vis Spectroscopy followed by Sol-gel preparation technique.

Theoretical background:

ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type.[7] This semiconductor has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. Those properties are valuable in emerging applications for: transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, and electronics as thin-film transistors and light-emitting diodes.

Zinc oxide crystallizes in two main forms, hexagonal wurtzite[17] and cubic zincblende. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn(II) given in figure(1)



a) Wurtzite Structure b) Zincblende Structure

Figure: 1 a) Wurtzite form and b) Zincblende form of ZnO

During the last years, ZnO thin films have been studied extensively due to their potential applications, as piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, conductive gas sensors, transparent conductive electrodes, solar cell windows, and varistors

Zinc oxide is a good candidate for evaluating the Tauc method because it has been widely studied for a number of useful applications [2–20]. Among these applications, the band-gap plays a central and fundamental role as it controls many absorption and conductivity phenomena. Single crystal optical studies have found a direct band-gap of 3.3 eV [21–23], though many of the papers surveyed in the present thin film analysis have collected data from very well crystallized films or even epitaxially grown layers.

Principle of Absorption Spectroscopy

This technique is based on the absorption of light by a sample. When a UV/Vis light is incident on the sample, the light is partially absorbed. The transmitted light is captured as a function of wavelength by a spectrophotometer, providing the samples UV-Vis spectrum. Depending on the amount of light and its wavelength absorbed by the sample, valuable information can be obtained, such as band gap, thickness, concentration and the purity of the sample.

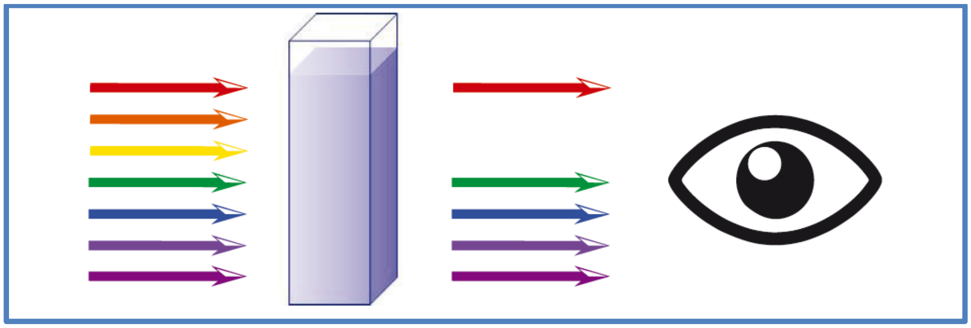


Figure 2: Light passing through a sample solution is partially absorbed by the components

Absorbance and Transmittance:

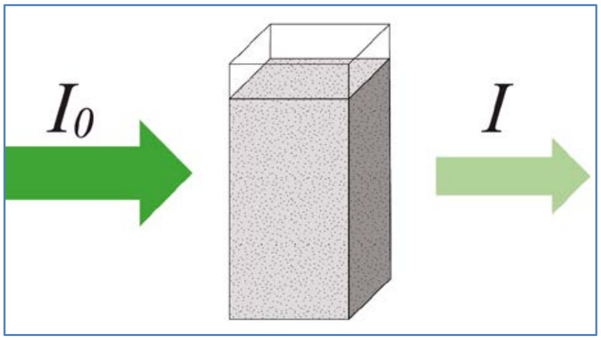


Figure 3: Light attenuation by absorption of sample molecules in solution

The ratio between the two intensities I/I_0 is defined as Transmittance T,

$$\mathbf{T} = \frac{I}{I_0}$$

The absorbance can be defined as **A= - log T**.

It is the negative logarithm of the transmittance value.

The band gap of the semiconducting materials is one of the critical parameters for semiconductor and nanomaterial's industries. It refers to the energy difference between the top of the valence band to the bottom of the conduction band. One can determine the band gap of semiconductor materials using UV-VIS absorption technique. In this experiment, we demonstrate how the band gap of a material can be determined by UV-Vis absorption spectrum.

Bandgap calculation:

We can also calculate the band gap of the materials using Tauc method as described below-

$$\alpha = \frac{A\left(hv - E_g\right)^n}{hv}$$

We can write this equation as;

$$(\alpha hv)^{1/n} = A^{1/n} hv - E_g A^{1/n}$$

$$\text{Where } \alpha = \frac{\ln\left(\frac{1}{T}\right)}{t}$$

α; absorption coefficient
T; Transmittance
t; Thickness of the sample
n; 2, 1/2, 2/3 and 1/3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions respectively.

Therefore by plotting the graph of $(\alpha\ h\nu)^{1/n}$ Vs. $h\nu$, we will get slope as $A^{1/n}$ and y intercept as $A^{1/n}\ E_g$. Dividing y intercept by A^{n}, we can estimate the band gap of the sample.

Requirements for the experiment:

A. Electrical equipment:

1. UV light source
2. Optical fiber
3. Spin Coater
4. Sample Holder
5. Hot Plate
6. Spectrophotometer

B. Materials:

1- Zinc acetate dihydarte
2- 2-Methoxy ethanol
3- Monoethanolamibe (MEA)
4- ITO coated Substrate/ Glass

Brief description of the experimental procedure:

Preparation of Zinc oxide solution:

The Zinc oxide solution (concentration 0.45 M), Zinc acetate dehydrate (0.66 g) as precursor materials was dissolved in 2- methoxy ethanol (6.4 ml) as a solvent. Further addition of controlled amount of monoethanolamine (MEA) (0.3 ml) as stabilizing agent has been added drop wise. The mixture was stirred for 12 hour at room temperature and a colorless solution of formed after 12 hours of stirring. (The preparation of solution has been already done by the lab staff before starting the experiment by students.)

Figure 4: Colorless Zinc Oxide solution

Thin film preparation:

For the thin film preparation on glass substrates, following steps should be followed-

1. Cut the glass slide in to desired shape using diamond cutter (2.5 cm square shape)
2. Clean the glass substrates with the soap solution using brush
3. Ultrsonicated all substrate with DI water, acetone and Methanol for 5 min each. Put them in oven at temperature 120 ^{o}C for 10 min.
4. Spin coat the zinc oxide solution using spin coater inside the yellow room at RPM 1500 for 1 min.
5. Anneal it at the temperature 300^{o}C in hot plate for 10 min.
6. Wait for 5 min to cool the substrate and again repeat the same procedure for 4 times.
7. Spin coat the zinc oxide solution four times on same substrate as above mentioned procedure.
8. The measured thickness of thin film is around 100 nm.

Characterization of Zinc oxide thin film

Absorption Measurement and Band gap Calculation:

1. For the absorption measurement of thin films, UV-Vis spectroscopy technique should be use.

2. Figure shows the experimental setup of UV-Vis spectroscopy technique.
3. Turn ON light source at least 10 min before the measurement to warm up the lamp
4. Open the Overture software installed on the computer
5. The lamp spectrum will be displayed in the computer screen
6. Set the integration time and smoothing value such that the peak is at about 85% of maximum range.
7. Put the uncoated glass substrate inside the thin film sample holder
8. Click on reference button on the software. It store your reference spectra
9. Click the copy data clipboard and paste it in excel sheet.
10. Now remove the optical fiber from spectrophotometer and close the room tube light and click on dark data button of the software. It will store your dark spectrum
11. Click on copy data button and paste it in excel sheet.
12. Now put the zinc oxide coated thin film in the sample holder and click the copy data button and paste copied data to excel sheet.
13. It is your sample spectrum data
14. Now Click on Absorption button and click on copy data and paste it in excel sheet. It will give the wavelength versus absorbance data.
15. Now You can also calculate your absorption data using the formula

$$\text{Absorbance} = -\log_{10}\left(\frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda}\right)$$

Where:
$S\lambda$; Sample intensity at wavelength λ
$D\lambda$; Dark intensity at wavelength λ
$R\lambda$; Reference intensity at wavelength λ

And transmittance as- Transmission % = $(S\lambda - D\lambda / R\lambda - D\lambda) \times 100$

Plot the graph Absorbance versus wavelength (280-600 nm) with 10 nm interval

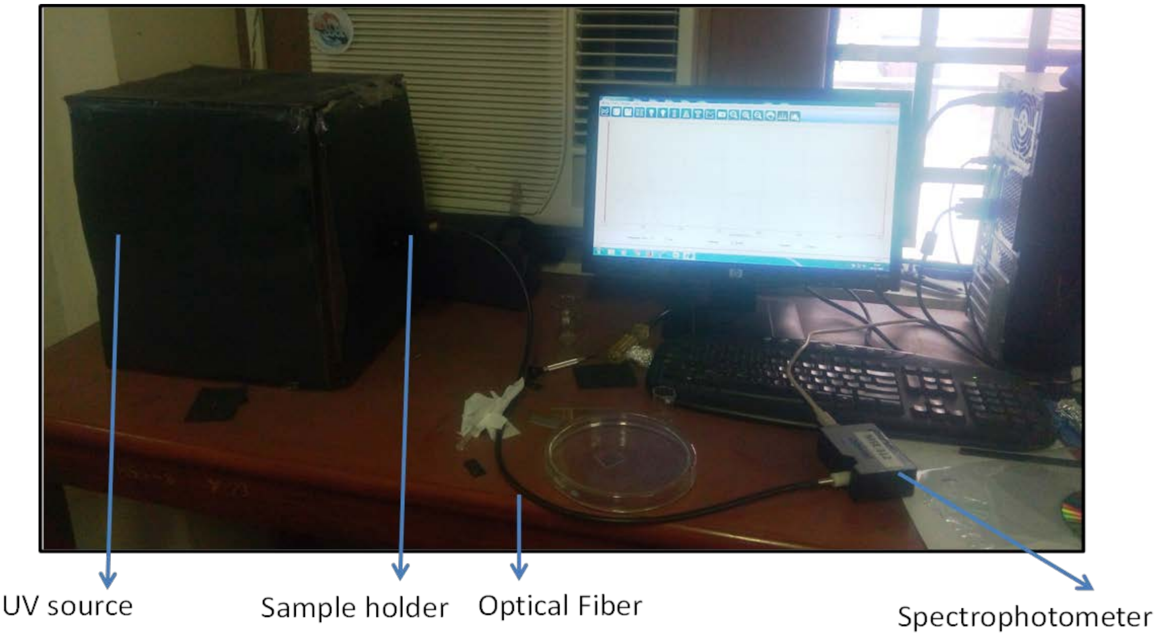


Figure 5: Experiment Setup for the Measurement of absorption spectra of Zinc Oxide thin Films

For the band gap calculation make a table given below and draw a graph (***Energy (hv) versus*** $(\alpha * hv)^{1/2}$) as mention above (Tauc Method).

Wavelength (280-600 nm)	**Absorbance(a.u)**	***Energy (hv)***	**$\alpha = 2.33 * A/\text{thickness}\ (t)$**	**$\alpha * hv$**	**$(\alpha * hv)^{1/2}$**

Results:

1. Absorption Spectrum of Zinc Oxide thin film
2. Report the calculated band gap of thin film
3. Report the Transmission spectra of thin films

References: