2.1 Introduction

The details of experimental technique used for the investigations presented in this work are described in this chapter. Experimental setups for a.c and d.c photoconductivity measurements, setup for electrical switching measurements, details of photoconductivity cell fabrication, technical details of x-ray photoelectron spectroscopy (XPS) measurements etc. are outlined in this chapter. The method of preparation of glass samples in the bulk form is also described. The results presented in chapters 3, 4, 5, 6 and 7 have been obtained by carrying out measurements employing the experimental techniques outlined in this chapter.

2.2 The photoconductivity setup

The basic requirements for a photoconductivity measurement setup are (i) a radiation source of sufficient intensity in the required spectral range, (ii) optical unit such as a monochromator to select the appropriate wavelength of the radiation for irradiating the sample, (iii) an intensity modulator such as an optical chopper for a.c measurements, if required, (iv) conductivity cell in which sample is mounted and irradiated with the light beam and (v) necessary instruments to measure the signal produced. A general schematic diagram of a typical photoconductivity setup is shown in Fig.2.1. A more detailed description of each of these units is given in the following paragraphs.
2.2.1 Radiation source and monochromator

Incandescent or arc lamps and lasers are the two popular types of light sources that can be used for photoconductivity measurements. High pressure Xe arc lamps, high pressure Hg lamps, tungsten lamps etc. are the commonly used polychromatic sources. There are two major classes of radiation sources used in photoconductivity measurements viz. incoherent sources and coherent sources.

Incoherent sources in u.v-vis-nir region tend to fall into the following two major categories (a) incandescent emitters (b) arc sources . The emission of an incandescent source can be approximated by radiation emanating from a black body at a given temperature. Tungsten lamp provides one of the simplest and most economical sources of continuous radiation throughout the visible and near infrared regions. The most popular incoherent source is the high pressure Xenon lamp. This lamp operates at pressures of 50-70 atm. and is a very efficient emitter of intense radiation from 230 to 700 nm. The most promising source of tunable coherent radiation in uv-visible region is a dye laser. A suitable monochromator can be used to select the appropriate wavelength of the radiation. Both prism and grating monochromators are popular. A suitable lamp-monochromator combination can provide continuous tunability of wavelength from the near infrared to the

Fig.2.1 A general schematic diagram of photoconductivity measurement setup
ultraviolet. Obviously, suitable optical elements need to be selected depending on the wavelength range of interest.

In our measurements the light sources used are a 300 W tungsten lamp and a 1 kW Xe arc lamp. A McPherson monochromator (Mod. 275) has been used for obtaining the desired wavelength for irradiating the sample. This monochromator has a concave holographic grating as the dispersive element and provides a resolution better than 0.1 nm.

2.2.2 Intensity modulator/Optical chopper
A mechanical chopper driven by a motor whose speed can be controlled precisely is the most popular light intensity modulator for a.c. photoconductivity measurements. Such choppers provide an almost 100% modulation depth. The optical chopper used in the present measurements is an SRS Model 540 which provides a maximum modulation frequency of 4 kHz. The chopper control unit provides a synchronous signal at the frequency of the chopper with which a lock-in amplifier can be triggered.

2.2.3 Photoconductivity cell
The photoconducting properties of bulk chalcogenide glasses have dependence on composition of the material, temperature, incident wavelength, intensity of light etc. [1]. In order to carry out these investigations systematically, a versatile photoconductivity cell has been designed and fabricated, the details of which are outlined below. A sketch of the cell is given in Fig. 2.2. Various parts of the photoconductivity cells are listed in this figure.

Photoconductivity cell mainly consists of the following parts (i) an outer chamber (ii) a cylindrical tube which acts as liquid nitrogen reservoir for the purpose of making low temperature measurements (iii) a sample holder and a glass window. The outer chamber is made of an M.S pipe of outer diameter 20 cm, thickness 6 mm and height 40 cm. M.S
Fig. 2.2 A schematic diagram of the photoconductivity cell

1) Sample holder, 2) Heater, 3) Glass window, 4) Heater supply, 5) Connector for temperature sensor, 6) Liquid nitrogen reservoir, 7) BNC connectors, 8) Connector to vacuum pump.

flanges are welded at the top and bottom of this pipe. The flanges have O ring grooves. The chamber is provided with a vacuum line which can be connected to a rotary pump so that the cell can be evacuated whenever necessary.

External electrical connections to the cell are provided through a port provided on the top of the plate of the chamber. This port is provided with four BNC connectors for
connections from the sample, a D-type connector for taking the signal from the temperature sensor and another connector for heater supply.

The liquid nitrogen reservoir is made of an SS tube which is welded at the center of the top plate. The sample holder which is made of copper is attached to bottom of this reservoir. Since copper is a good thermal conductor with a high value for specific heat capacity, temperature gradients will be minimum across the sample holder. The mass of the sample holder is a critical factor in controlling the temperature. High thermal mass enables one to achieve in very slow rates of heating and cooling. The mass of the sample holder is evaluated after considering the specific heat capacity, power delivered by the temperature controller to the heater, the required rate of rise of temperature and the heat loss from the different portions of the unit. The quantity of liquid nitrogen required to cool the sample to 77 K is also a factor while designing the system for doing low temperature measurements.

2.3 Measurement of photoconductivity

Photoconductivity measurements can be carried out either by d.c (steady state) method or by a.c (pulsed excitation) method. These two methods are described separately in the following paragraphs.

2.3.1 d.c Method

In the steady state method, the dark current ($I_d$) and the d.c photocurrent under steady state illumination ($I_{ill}$) are measured. The photocurrent ($I_{ph}$) is given by

$$I_{ph} = I_{ill} - I_d.$$  

The block diagrams of the experimental setups for measuring d.c photoconductivity are shown in figures 2.3 and 2.4. It can be done either by the two probe or the four probe method depending on the resistivity and geometry of the sample. Contact resistance can be neglected in the case of samples with high resistivity and two probe technique is
sufficient if the sample has a regular shape. For samples with low resistance, contact resistance cannot be neglected and for them four probe technique is preferred. This method eliminates the effect of contact resistance. Moreover, this is more suitable for samples without a definite geometrical shape. The resistivity of a small area specimen is given by \( \rho = 2\pi \delta R/\ln 2 \) where \( \delta \) is the thickness of the sample[3]. Of the four probes available, two are used to pass a steady current through the sample and the other two are for measuring the voltage generated across the sample. The larger or thinner is the sample, the closer can the voltage probes be placed to the current probes, in which case the

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Fig.2.3 Experimental setup for two probe method for measuring d.c photoconductivity
conductivity of the sample can be measured accurately. Area of contact of the electrodes on the sample should be small compared to the distance between the contacts.

Fig.2.4 Experimental setup for measuring d.c photoconductivity by four probe method.

Since most of our samples are having high resistivity values of the order of $10^8$ ohm-m, two probe technique has been adopted for measurements. The samples are polished and shaped to exact square or rectangular shapes. The electrodes can be connected either in coplanar or sandwich mode. In our measurements for bulk samples the sandwich
configuration has been used. The sample is sandwiched between two conducting glass plates which are SnO₂ coated. In this arrangement the sample can be illuminated through one of the electrodes. The contacts are found to be ohmic from a study of the V-I characteristics of the contacts.

A Keithley autoranging picoammeter (Model 485) is used for current measurements. The incident power is measured using a KINMON power meter (Model PT-3000)

2.3.2 a.c Method

The a.c method has certain advantages over the steady state (d.c) method. This method eliminates the effect of any stray light, dark current or any other unmodulated signal or any signal modulated at any other frequency [4-6]. Chopped radiation from a 1kW Xe arc lamp (Spectroscopy Instruments) has been used as the excitation source. An SRS 830 DSP lock in amplifier is used for measuring photocurrent signals. The chopping frequency of incident light is fed to the lock in amplifier for its synchronization. The block diagram of the setup for a.c method is shown in Fig.2.5.

**Carrier lifetime from a.c photoconductivity measurements**

The lifetime of generated carriers can be obtained from a.c photoconductivity measurements by frequency resolved photocurrent (FRPC) measurements. In FRPC the photocurrent is measured by varying the chopping frequency of incident light from 1 Hz onwards and the frequency vs photocurrent plot is drawn. It can be found that the photocurrent attains a threshold maximum value for a particular frequency \( f_{\text{max}} \) above and below which the photocurrent shows lower values. The carrier lifetime \( \tau \) is then given by

\[
\tau = \frac{1}{2\pi f_{\text{max}}}
\]
While studying the spectral dependence of photoconductivity with a lamp monochromator system, there is the problem of spectral variation of source intensity. This should be normalized to get the exact spectral behaviour. The power of the incident radiation \( P_{\text{inc}} \) is measured for this end. Then by knowing the wavelength \( \lambda \) of incident radiation, the variation of photocurrent with wavelength can be normalized. If \( I_{\text{ph}} \) is the photocurrent, then the normalized photocurrent is given by \( (I_{\text{ph}}/q) / (P_{\text{inc}} \lambda /hc) \). Actually this quantity gives the quantum efficiency of the sample at that incident wavelength.

**Spectral variation of photoconductivity**

Fig. 2.5 Block diagram of the a.c photoconductivity measurement setup
2.4 Electrical Switching Measurements

The block diagram of experimental setup used for electrical switching measurements in amorphous semiconductor samples is shown in Fig.2.6. [7]. Basically, electrical switching measurement setup is the same as that of electrical conductivity. Care is taken to ensure that one of the contact terminals is of pointed type. This is essential to ensure the reproducibility of results.

In order to get the V-I characteristics, a known current is sent through the sample from a constant current source. The voltage developed across the sample is measured by a digital voltmeter. The current through the sample is varied from low values to higher

![Block diagram of experimental setup for electrical switching measurements.](image)
values in steps and the V-I characteristics are plotted. The pointed electrode is positioned at different points on the surface of the sample and measurements are always repeated to check the reproducibility.

Initially the current and voltage show the linear variation (ohmic behaviour). For a particular value of current, the voltage across the sample attains a threshold ($V_t$) value. Further increase in current results in a decrease of voltage and the sample deviates from the ohmic behaviour to a negative resistance region which leads to a high conducting state.

2.5 X-ray photoelectron spectral analysis (XPS)

Surface analysis of a material by XPS involves irradiation of the sample in vacuum with monoenergetic soft x-rays and sorting the emitted electrons by energy. The spectrum so obtained is a plot of the number of emitted electrons per energy level versus their kinetic energy. Each element has unique elemental spectrum and the spectral peaks from a mixture are approximately the sum of the elemental peaks from the individual constituents. Since the mean free path of the emitted electrons is very small the electrons which are detected originate from only the top few atomic layers of the sample[8,9]. A schematic representation of a typical XPS machine is given in Fig.2.7. Since XPS measurements are very delicate and highly sensitive to impurities and environmental changes, extreme care should be taken while recording the spectrum. Some of the relevant points to be taken care of are outlined below[10-11].

Mounting of the sample

In majority of XPS applications sample preparation and mounting are not critical. Typically the sample can simply be mechanically attached to the specimen mount and analysis begin with the sample in the as received condition. Sample preparation is even discouraged in many cases especially when the natural surface is of interest, since almost all procedures will tend to modify the surface composition. Ordinarily any volatile
material must be removed (if there is no special interest in the volatile material) from the sample before analysis. Removal of volatile material can be done by a long term pumping in a separate vacuum system or by washing it with a suitable solvent.

Ion sputtering, etching or other erosion techniques such as use of oxygen atoms on organic materials, can also be used to remove surface contaminants. Argon-ion etching is also commonly used to obtain information on composition as a function of depth into the specimen.

**Calibration of the XPS machine**

To ensure the accuracy of the XPS data the instrument is calibrated regularly throughout the data gathering process. The energy scale is periodically calibrated using a high

![Diagram of an XPS machine](image)

**Fig.2.7** A general schematic diagram of an XPS machine
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precision digital voltmeter. The best way to check the calibration is to record suitable lines from a known conducting specimen. Typically the $\text{Au}_{4f}$ or $\text{Cu}_{2p}$ lines are used for calibration. The lines should be recorded with a narrow sweep width in the range of 5-10 eV and pass energy of 20 eV or less. The peak position is determined accurately by drawing cords parallel to the baseline and drawing the best straight line or simple monotonic curve through the midpoints of the cords.

For the measurements presented in this work, the XPS machine used is a VG Scientific Ltd. (UK). The radiation used is MgK$\alpha$.

2.6 Preparation of samples

Bulk glass of the required material is prepared by the conventional melt quenching technique[8-9]. Spectroscopically pure (99.999%) constituent elements are weighed in appropriate proportions. These are taken in a quartz ampoule, evacuated and sealed. The ampoule is then kept in a rotary furnace for nearly 24 hours at a temperature well above the melting point of the constituents. There is provision for periodic rotation and by this the melt get mixed uniformly. The ampoule is then quenched in ice water. The cooling rate is around $500^\circ$ C per second. Then the ampoule is annealed for nearly one hour at a temperature below the glass transition temperature of the sample. The amorphous nature of the sample is checked by X-ray diffractometry. The sample is then cut and polished so that it has definite geometrical shape.
2.7 References