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Characterization Techniques Of Zno Thin Films

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ABSTRACT:

ZnO has a hexagonal wurtzite structure in which each cation is surrounded by four anions and vice versa. Non-centrosymmetric ZnO structures are one of the most essential qualities that make ZnO suitable for piezoelectric and pyroelectric applications because of its tetrahedral coordination structure. Optoelectronic devices, sensors, transducers, catalysis, and medicinal devices all benefit from the unique properties of ZnO thin films and nanostructures. In this article, characterization techniques of ZnO thin films were highlighted.

Keywords: ZnO, Thin, Flims, Characterization

INTRODUCTION:

The characteristics of ZnO thin films and nanostructures are studied using a variety of characterisation methods. Analysis of structural, morphological, compositional, and spectroscopic properties is done using X-Ray Diffract meter (XRD), Atomic Force Microscope (AFM) or Field Emission Scanning Electron Microscope (FESEM), and Raman spectroscopy. Optical and electrical properties are measured using UV-Visible spectrophotometers, respectively, and electrical properties are measured using a voltage metre. X-Ray Photoelectron Spectroscopy is used to determine the elemental composition and oxidation state (XPS). Sun simulator with Keithley source metre and AM 1.5 conditions is used to evaluate solar cell current-voltage characteristics.

X-RAY DIFFRACT METER:

W.C. Roentgen discovered X-rays by accident in 1895. These are electromagnetic waves with a wavelength of less than 0.1-1 Angstroms, which are very short. As the X-ray wave length approaches the size of atoms, this method is seen as a flexible means of figuring out the crystal structure of substances. Laue discovered in 1912 that X-rays may diffract through crystals.

The distance between lattice points in a crystal is about the same as the size of an atom or molecule, which is around a few angstroms in diameter. In the case of X-rays, diffraction is noticed because they have a wavelength of this size. Aside from crystal structure determination, the XRD method has several additional applications, including chemical analysis, stress measurement, phase equilibria, and the measurement of particle size [1].

When a crystal is bombarded with a monochromatic beam of X-rays at a certain incident angle, intense reflected X-rays are produced when the wavelengths of the scattered X-rays are interfering constructively due to the periodicity in the atomic arrangement. When this constructive interference occurs, a diffracted beam of X-rays leaves the crystal at an angle equal to that of the incident beam. The general relationship between the wavelength of the incident X-rays (λ), the angle of incidence (θ) and spacing between the crystal lattice planes of atoms (d) is known as Bragg's law, expresses as

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

The Seifert Analytical X-Ray diffractometer uses Cu-K radiation with a wavelength of 0.15418 nm to identify the crystalline type and average crystallite size of ZnO-based thin films and nanostructures. Figure shows a typical X-ray diffraction pattern at the atomic planes.

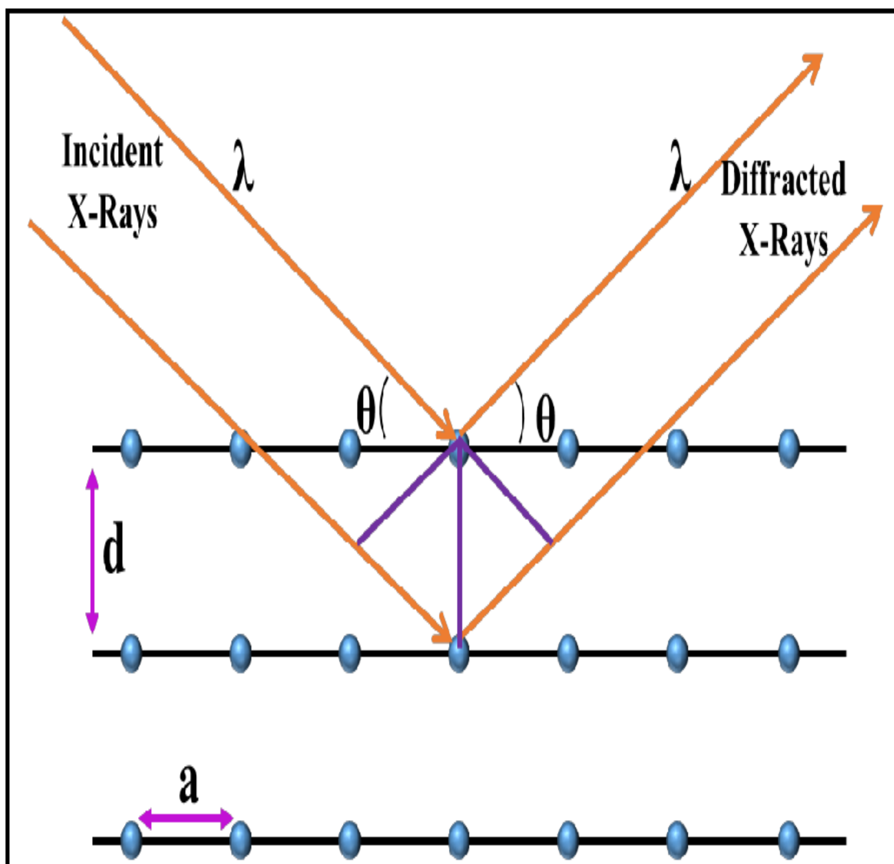

Figure 1. Diffraction of X-Rays Through Planes of Crystal

ATOMIC FORCE MICROSCOPE:

The surface topography may be studied with the Atomic Force Microscope (AFM) independent of the material's conductivity. Cantilever has a sharp point with a radius of less than 50 nm attached to one end. It's as if a phonograph needle is slicing through the groove of a record while the force exerted at the tip remains constant. A laser beam is reflected off a mirror mounted to the top of the needle and an interferometer is used to properly measure the distance travelled by the laser beam and therefore the location of the tip is recorded. It's easy to see how an AFM works by looking at Figure [2].

A Veeco Dimension V SPM atomic force microscope is used to analyse the surface morphology and Root Mean Square (RMS) roughness of the sputter-deposited and chemically etched Al doped ZnO and Ga doped ZnO thin films.

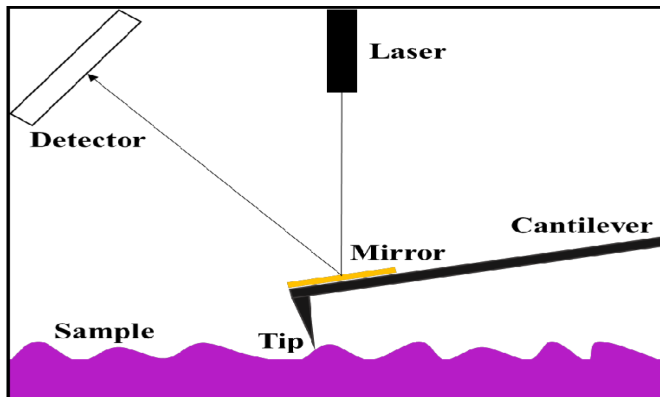

Figure 2. Basic Components of an Atomic Force Microscope

FIELD EMISSION SCANNING ELECTRON MICROSCOPE:

Microstructure morphology may be studied using the FESEM, one of the most versatile equipment on the market. optical microscopy is limited to a resolution of around 200 nanometers (nm). As a result of multiple studies showing that an electron may be deflected by a magnetic field, a high-energy electron beam has been used as the light source in electron microscopy development ever since. Various signals are generated at the surface of solid objects using a focussed beam of high-energy electrons in a SEM [3]. Through the analysis of the signals generated by electron-sample interactions we may learn about the sample's shape, composition, crystalline structure, and even its direction in space. One or two condenser lenses concentrate an electron beam with energy ranging from a few hundred eV to 100 KeV on a spot with a diameter of 0.4 nm to 5 nm.

Figure 3. Photograph of Field Emission Scanning Electron Microscope

Scanner coils or deflector plates in the electron column generally in the last lens deflects the beam such that it scans across a rectangular region of sample surface, as seen in this figure. To begin with, the main electron beam interacts with a teardrop-shaped portion of the material known as the interaction volume, which spans from less than 100 nm to roughly 5 m under the surface. The electron landing energy, specimen atomic number, and specimen density all have a role in determining the interaction volume's size. Energy exchange between electron beam and sample results in reflection of high-energy electrons, emission of secondary electrons, and emission of electromagnetic radiations, each of which may be detected by specialised detectors. The thermionic emission of electrons from the electron gun reduces the SEM's efficiency to a significant degree. Because of this, SEM is beneficial in studying material at lower magnifications. The electron gun's field emission of electrons may bypass this barrier, allowing for magnifications in excess of 2000X and atomic level examination.

The sputter deposited doped ZnO thin films and the hydrothermally grown ZnO nanostructures are recorded using a Field Emission Scanning Electron Microscopy (FESEM, Carl Zeiss - Neon 40) and Energy Dispersive X-ray analysis (EDX).

UV-VISIBLE SPECTROPHOTOMETER:

It is vital to understand how electronic transitions occur between energy bands by studying the optical characteristics of materials in the UV-Vis-NIR (UV-Vis-NIR) range. An optical prism or diffraction grating breaks a light beam into its component wavelengths. Each monochromatic beam is divided into two equal-intensity beams by a half-mirrored device in turn. A single beam of light travels through a tiny, transparent container carrying the sample.

The reference substrate is scanned by the opposite beam." With an electrical detector, we can measure the resulting intensities of these two light beams, one being broadcast and the other being received. What's known as a "reference" beam is defined as I0; what's known as

a "sample" is defined as I. Scan of all wavelengths takes place over a short period of time. Because the absorption varies with wavelength, a material's properties are reflected in its absorption patterns. One way to compute absorbance is by using the Beer-Lambert principle.

Perkin Elmer Lambda 650 UV-Visible spectrophotometers were used to measure the total, diffused, and direct transmission spectra of the sputter-deposited AZO and GZO thin films in the wavelength range from 200 to 1100 nm [4].

It was found that ZnO nanostructures had a photocatalytic capability that was explored by analysing the absorption spectra of dye degradation using a UV-visible spectrophotometer. As a model system, ZnO nanostructures formed in different pH precursor solutions photocatalyze the degradation of rhodamine B (N, N, N', N'-tetraethylrodamine) under UV light. Using fluorescent 365 nm UV-light illuminations, we explore the absorption spectrum changes that occur sequentially during Rhodamine B photocatalytic decolonization.

Figure 4. Photograph of UV-Visible Spectrophotometer

THICKNESS MEASUREMENT:

The thickness of any thin film is the most basic metric that offers an idea of the rate of deposition and is the most important in the fabrication of semiconductor devices. It is necessary to know the thickness of the deposited films in order to determine optical and electrical characteristics such as bandgap and resistivity. It is possible to measure the thickness of thin coatings on a flat substrate using a stylus type surface profilometer (Dektak XT, Bruker). A transducer transforms the mechanical leap of the stylus from the film's surface to the substrate into an electrical signal. For the purpose of determining the

film's thickness, this electrical signal is continuously monitored. Figure shows an image of the thickness profiler.

Figure 5. Photograph of Thickness Profilometer

CRYOSTAT SYSTEM:

In terms of electronic transport, the electrical conductivity of a substance serves as a gauge. On Corning glass substrates, the dark and photoconductivity of films formed on Keithley 6487 picoammeters are measured. Using a cryostat (CMT 25, HHV India), thin films are put in a vacuum setup and a heating system to be monitored. Turbo molecular pumps, rotary pumps, and liquid nitrogen traps may all work together to create a vacuum of around 10-5 torr. Mounting the samples using silver paste on copper blocks ensures a good thermal contact, and a heating coil is inserted in the copper block holders to achieve the necessary temperature (from liquid Nitrogen temperature to 500K). For connection, we use a thermal evaporation technique to deposit the aluminium contacts.

Measurements of dark and photocurrent in undoped and doped amorphous silicon thin films may be made using this equipment. By exposing the samples to light and photogenerated carriers, the photocurrent of the samples is measured and compared to the dark current. Current measurements in relation to temperature may be used to determine the amorphous silicon layers' activation energy [5].

Figure 6. Photograph of Cryostat System

HALL MEASUREMENT:

Electromagnetic fields applied perpendicular to a current-carrying wire generate voltages in a path perpendicular to both the current and the magnetic field across a specimen. The phenomenon is known as the Hall effect, and the voltage that results from it is referred to as the Hall voltage. Physicist Edwin H. Hall discovered the Hall effect in 1879 and named it after him. It is from this formula that the Hall coefficient RH may be computed

$$R_H = \frac{V_H . b}{I H_z}$$

It is therefore possible to compute the Hall coefficient (RH) in this manner, using just the values of I (frequency) and Hz (intensity).

The relation between Hall coefficient (RH) and mobility (μ) is defined as,

$\mu = RH\ \sigma$

where σ is the conductivity.

The Hall effect measurement provides the following information:

i. Electrons or holes as charge carriers are identified.

ii. Charge carriers per unit volume are counted in order to establish the carrier concentration.

iii. The charge carrier's motion is directly measured.

iv. The resistivity and resistance of the sheet are measured.

The Ecopia HMS 5000 Hall measuring apparatus measures the most essential electrical characteristics of semiconductors, such as carrier concentration, sheet resistance, resistivity, conductivity, and mobility of AZO and GZO films produced at varied process settings. Fig. shows the Hall effect and measuring system schematic.

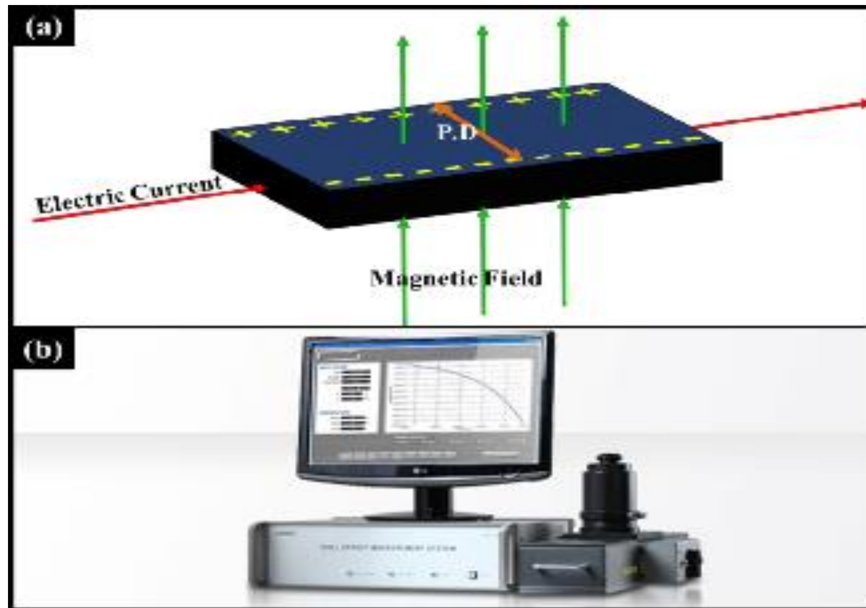

Figure 7 (a) Schematic of Hall Effect and (b) Ecopia HMS Hall Measurement System (Source: Bridge Technology)

FOURIER TRANSFORM INFRARED SPECTROSCOPY:

It stands for Fourier Transform in the abbreviated form FTIR. Using a Fourier Transform, an interferometer's intensity time output may be transformed into a recognisable infrared spectrum for use in spectroscopy. The energy of infrared radiation is equal to the difference between the vibrational modes of a molecule's vibrational energy landscapes. Consequently, infrared spectroscopy serves as a means of determining the molecules' vibrational motion. Because of the limitations of IR spectroscopy, not all vibrations can be detected. Only vibrational transitions accompanied by a change in the dipole moment may be observed since the approach uses electromagnetic radiations to interact with the molecule [6].

An organic or inorganic substance's molecular structure or chemical bonding may be uncovered by FTIR investigation. In failure analysis, it is utilised to find new materials in a specimen that were previously unidentified. For the process to function, bonds and groups of bonds vibrate at distinct frequencies. It is the frequency of the infrared photons that a

molecule absorbs that is unique to that molecule. FTIR spectroscopy was used to analyse ZnO nanostructures in the range of 400–4000 cm-1 (Bruker, Alpha T) as illustrated.

Figure 8. Photograph of FTIR Spectrometer

RAMAN SPECTROSCOPY:

Radiation energy is dispersed when a ray of light passes through a material. Radiation of the incoming energy, as well as discrete frequencies above and below it, will be scattered in large quantities when monochromatic radiation or radiation with a very limited frequency range is employed. When we increase the wavelength, we see an increase in the Rayleigh scattering intensity. Because of this, a polychromatic incoming beam will scatter more of its smaller wavelength components than its longer wavelength components. Because of this, the sky seems blue. Except for Rayleigh scattering, some light is dispersed with a different frequency than the original light. These scatterings are being referred to as Raman scattering. The molecules' vibrational energy levels are reflected in the change in the spectrum's frequency range. As with IR spectroscopy, Raman scattering measures the frequencies of the scattered light rather than the absorption of the incoming radiation, hence it is a method for probing the molecule's vibrational states. In the case of anti-stokes scattering, the dispersed light has a higher frequency, whereas in the case of stokes scattering, it has a lower. The anti-stokes lines are weaker than the Stokes lines because they can only be noticed when a vibrational mode is thermally stimulated. The vibrational energy of a mode is represented by the difference in frequency between incoming and dispersed light [7].

ZnO nanostructures grown by hydrothermal method were studied using micro-Raman and photoluminescence (PL) methods by Renishaw and inVia (using excitations of Ar+ and He-Cd lasers at 514.5 nm and 325 nm, respectively) with a 100 objective and an 1800 gr/mm grating and thermoelectrically cooled CCD detector.

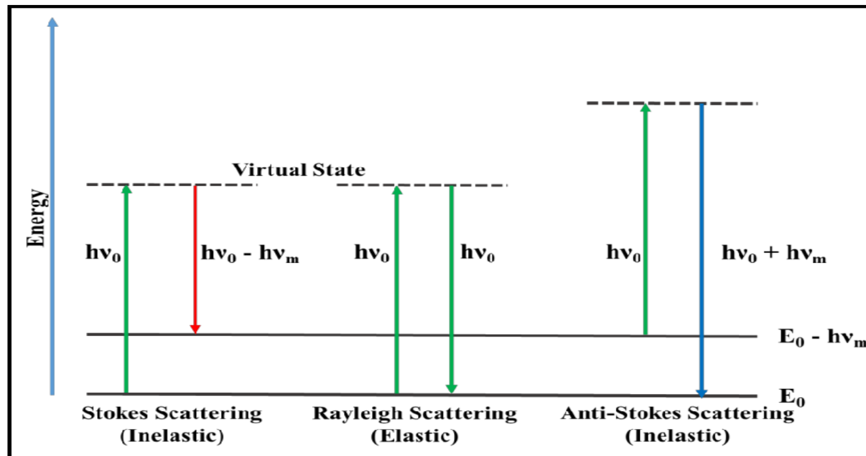

Figure 9. Band Diagram of Raman Effect

PHOTOLUMINESCENCE:

When a material absorbs and emits photons, it is called photoluminescence. To put it another way, it may be regarded as a rise in energy, followed by the emission of a photon. The term luminescence refers to the emission of light by a substance by any method other than the blackbody radiation. If you stimulate your body, you may cause your body to release light in several ways. As an example, cathodoluminescence describes emission that occurs as a consequence of electrical stimulation. High-energy photons may also be utilised to stimulate the sample in x-ray fluorescence. Photo excitations are a distinguishing feature of this luminescence type. However, this may be prolonged to minutes or hours even though the time between absorption and emission is normally in the range of 10 nanoseconds or less. As a final outcome, quantum mechanics laws govern chemical energy levels and allowable state transitions, resulting in preferentially absorbed or emitted light wavelengths [8].

Processes such as photoluminescence are critical in evaluating semiconductors for their purity and crystalline clarity. Through the use of photons to produce excited electronic states in a material system and a careful examination of the optical emission, photoluminescence (PL) may be used to determine the physical and chemical characteristics of materials. Contactless and nondestructive, it may be used to investigate the electronic structure of materials. An advantage of PL is its ability to examine extremely minute amounts or low concentrations, making it an excellent choice for a wide range of research applications. Quantity concentration determination is difficult unless circumstances are tightly controlled, therefore many PL applications are purely qualitative.

X-RAY PHOTOELECTRON SPECTROSCOPY:

X-Ray Photoelectron Spectroscopy (XPS) is a powerful characterization tool for the analysis of the surface chemistry of materials. XPS works on the principle of the

photoelectric effect, in which X-rays are used as the photon source to excite electrons. The illustration of the photoelectron emission and the equipment schematic is given in Figure. The kinetic energy of the emitted photoelectron (Ek) is the difference between the incident photon energy (hν) and the binding energy (Eb) of the core-level electron. From the known incident photon energy and the emitted electrons kinetic energy, the binding energy of the emitted electron can be calculated from the equation,

$$Eb = h\nu - Ek - \phi$$

The instrument's work function is represented by the symbol. Each element has a unique binding energy for the electrons in its atoms, therefore the element on a substance may be identified.

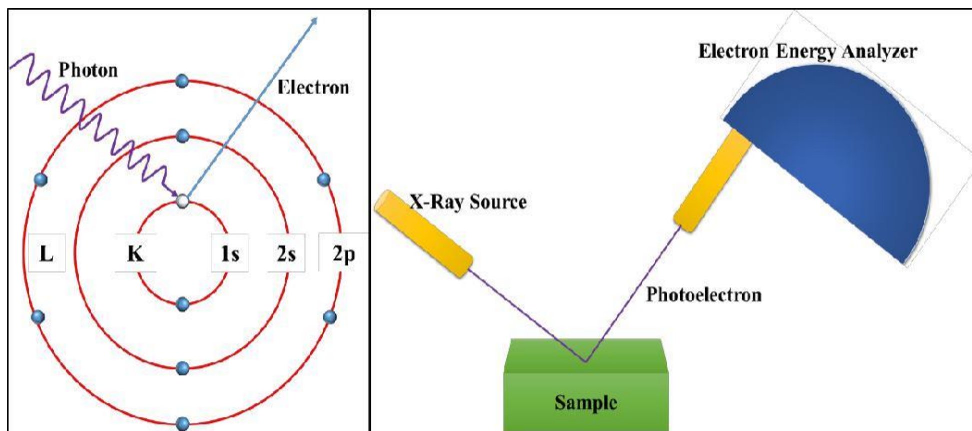

Figure 10. Schematic of Photoelectron Emission and XPS Instrument Setup

SOLAR CELL CHARACTERIZATION:

In order to manufacture a-Si:H solar cells, the p-i-n or n-i-p configurations must be used. To create the potential across the I layer, the doped p and n layers are responsible. P-n junction diodes are used in both solar cells and diodes because of their identical current-voltage characteristics under optimal operating conditions. There are shunt (RSh), series (RS), and load resistances in Figure, which is the equivalent circuit of a p-i-n solar cell (RL). electron-hole pairs are formed more often in the I layer when the I layer is illuminated. The p-layer is positively charged, while the n-layer is negatively charged, since the bulk of holes and electrons have migrated to the p-layer. As long as the external circuit is linked, electrons will ultimately flow through it.

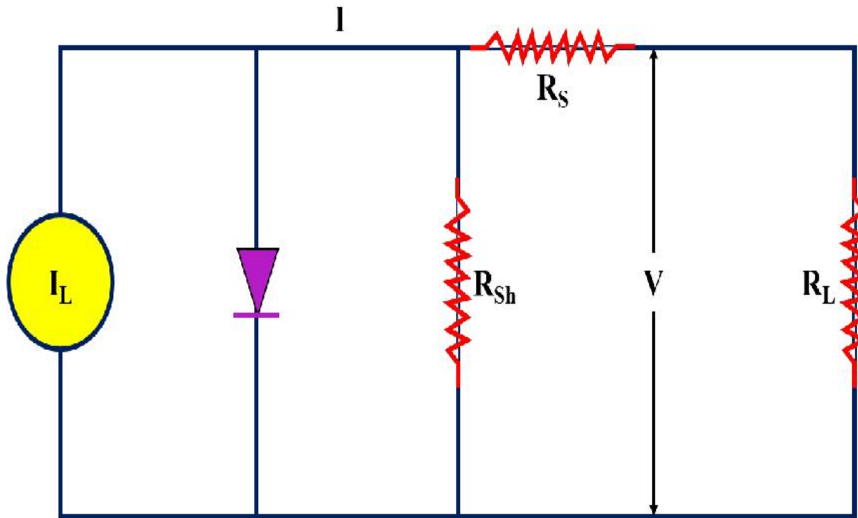

Figure 11. Equivalent Circuit of a-Si:H Solar Cell

I-V CHARACTERISTICS OF SOLAR CELL:

A sun simulator (ScienceTech Inc., Canada) is used to simulate a single sun situation in the lab in order to determine the I-V properties of solar cells. For a power density of 100 mW/cm2 at 25°C, this sun simulator's spectrum has an Air Mass of 1.5 (AM 1.5). Sunlight at an angle of zenith of 48.2 degrees is represented by this AM 1.5. The solar cell acts like a diode in a dark environment. Electricity is generated as soon as light strikes the solar cell device. Figure depicts the current-voltage characteristics of a solar cell (scale in 4th quadrant).

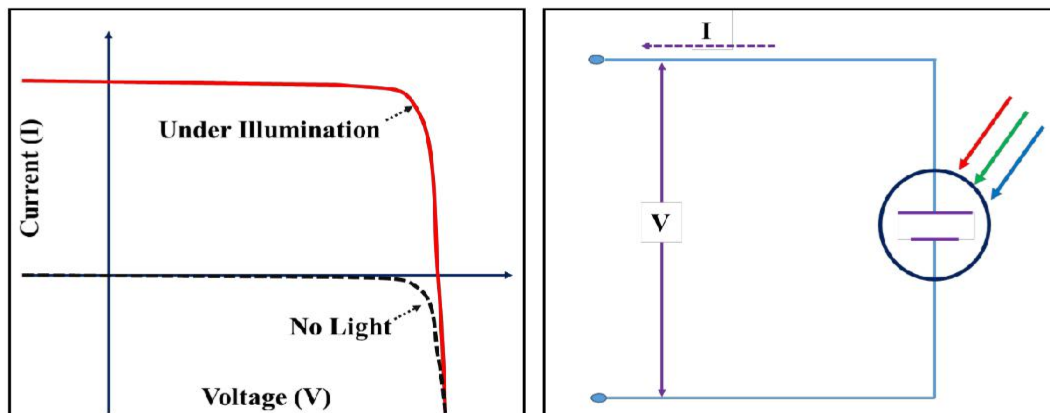

Figure 12. Current-Voltage Characteristics of Solar Cell and Associated Electrical Diagram

Short circuit current (Isc), open circuit voltage (Voc), fill factor (FF), and efficiency () are used to assess and evaluate the performance of solar cells. Under light, the curve of the

solar cell may be seen in Figure 2.18.. It can be seen in Figure that the solar cell's properties were measured using a sun simulator. At AM 1.5 circumstances, a AAA Sun simulator (Science Tech, Canada) connected with a Keithley source metre is used to measure the current and voltage characteristics of a-Si:H solar cells manufactured by PECVD [9].

(i) **Short Circuit Current (Isc)**: Maximum current through a solar cell when the terminals at n- and p-sides are shorted is this value. According to this formula, the value of Voc is 0. Because there is no voltage present, the short circuit current is nothing more than light-generated current. The current density (Current per unit area, mA/cm2) is often used to express this.

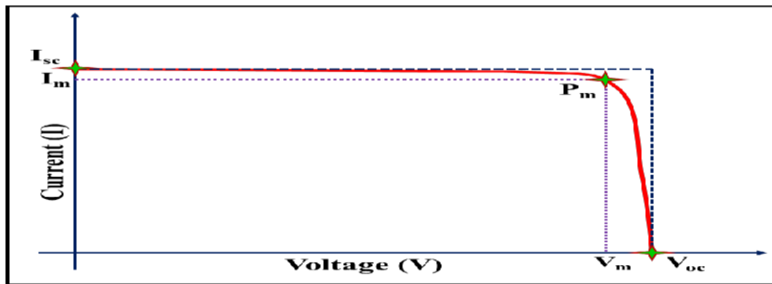

Figure 13. Typical Plot of a Solar Cell I-V Curve and its Parameters

(ii) Open Circuit Voltage (Voc): When the terminals open, the solar cell generates its maximum voltage. Isc then becomes zero. Reverse saturation current and light produced current affect open-circuit voltage, which in turn affects the voltage.

(iii) Fill Factor (FF): P0 = Voc Isc is defined as the optimum power, while Pm = Vm Im is the maximum power that can be recovered from a solar cell.

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \quad (1.6)$$

(iv) Efficiency (η): The ratio of the output power to the input power is known as the efficiency. For example, a solar cell's maximum power point (Pm) is a function of its input power (Prad). Prad is defined as 100 mW/cm2 or 1000 W/m2 in accordance with the international standard for solar cell characterisation.

$$\eta = \frac{V_{oc} \times I_{sc}}{P_{rad}} FF$$

Figure 14. Photograph of Sun Simulator with I-V Tester

CONCLUSION:

Metal Oxide (MO) semiconductors are among the world's most widely accessible materials. Unlike conventional group-IV inorganic semiconductors like silicon and germanium, their structural, electrical and optical properties have drawn the attention of many researchers around the world, and remarkable advancements in both technological advancements and industrial applications have been reported in the last few years [10]. These materials have a band gap that may be adjusted to display metallic, semiconducting, and insulating characteristics. Because of ZnO's low toxicity, thermal stability, strong oxidation resistance, large specific area, and high electron mobility, it has been widely used in optoelectronic devices.

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