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A Review Of Characterization Tools And Techniques For Nanomaterials And Nanocomposites

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ABSTRACT

The heterogeneous/hybrid materials known as nanocomposites are created at the nanometric scale by combining polymers with inorganic solids (such as oxides or clays). It is discovered that their structures are more intricate than those of microcomposites. The characterization of nanomaterials is important for understanding their properties and applications. This review describes the instruments and experimental setups utilized for various measurements towards the characterization of the synthesized nanocrystals. The techniques adopted to characterize the nanoparticles are X-ray diffraction (XRD), SEM, EDX, TEM, DC-Conductivity, Particle Size analyzer (PSA), UV – Visible Spectroscopy, Thermo Gravimetric Analysis/Differential Thermal Analyzer (TG/DTA).

Keywords: Nanomaterials, XRD, SEM, EDX, TEM, DC, PSA, UV, TG/DTA

INTRODUCTION

Nano-scale science and technology is a young and burgeoning field that encompasses nearly every discipline of science and engineering [14]. With rapid advances in areas such as molecular electronics, synthetic biomolecular motors, DNA-based self-assembly, and manipulation of individual atoms via a scanning tunneling microscope, nanotechnology has become the principal focus of a growing cadre of scientists and engineers and has captured the attention and imagination of the general public [3]. This field is defined primarily by a unit of length, the nanometre at which lies the ultimate control over the form and function of matter. The fundamental nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range, but measuring this nano dimension is not a very easy task. Although research is going on to synthesize nanostructured and nanophasic materials, characterizing these nanosized materials is also an emerging field posing a lot of challenges to scientists and technologists. Thus nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano-characterization techniques to allow better control of morphology, size, and dimensions of materials in the nano range [4]. The important characterization techniques used for nanotechnology research in various applications have been discussed in this paper.

TECHNIQUES TO CHARACTERIZE MATERIALS

Electron microscopy. This method examines the structure and composition of materials at a very small scale using an electron microscope.

- X-Ray Diffraction Analysis.
- Spectroscopy Analysis.
- Thermogravimetric Analysis.
- Mechanical Vibration Analysis.

X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive type of analytical technique that provides valuable insight into the lattice structure of a crystalline substance like unit cell dimensions, bond angles, chemical composition, and crystallographic structure of natural and manufactured materials [1]. XRD is based on the principle of constructive interference of X-rays and the sample concerned which should be crystalline. The X-rays which are generated by a CRT are filtered, collimated, and then directed towards the sample. The interaction that follows produces constructive interference based on Bragg's law which relates the wavelength of the incident radiations to the diffraction angle and lattice spacing.

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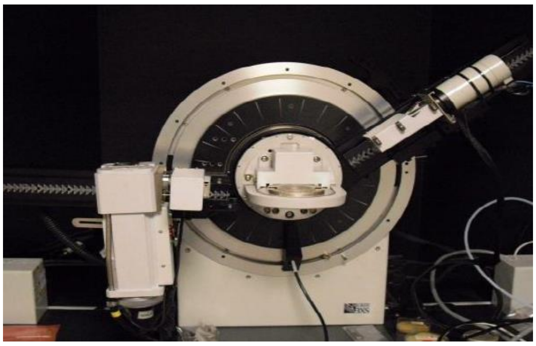

Fig.1: XRD-Equipment

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of the crystalline material and can provide information on unit cell dimension and atomic spacing. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident monochromatic rays with the sample produces constructive interference (and diffracted ray) when the condition satisfies Bragg's Law $n\lambda = 2d \sin\theta$ This equation relates the wavelength (λ) of electromagnetic radiation to the diffraction angle (θ) and the lattice spacing (d) in a crystalline sample by scanning the sample through the arrangement of 2θ angles. All the possible diffraction directions of the lattice are attained due to the random orientation of the powdered materials. X-ray diffraction (XRD) can be performed by an X-ray diffractometer machine as shown in Fig. 2. It is basically for the atomic arrangement in the crystal lattice. This technique is very preferable due to its d-spacing and order wavelength in Angstrom (Å). This basic component of the diffractometer is an X-ray coherent source, CuKα, 0.15418nm, and an X-ray beam directed towards the crystal and a detector that detects the intensity of the diffracted beam. Whereas other components are like focusing optics, sample holders, and rotating stands. The X-ray diffractometer software provides a range of intensities. Whereas the intensity of the diffracted X-rays is a function of d-spacing/2θ that peaks at a certain position. For a certain material, the XRD pattern is used as a signature and these signature patterns are provided by the Joint Committee on Powder Diffraction Standard (JCPDS). The information from these patterns is like crystalline phases, degree of crystallinity, amount of amorphous centers and microstrain, size, and orientation of crystallites [9-11]. The crystalline size (D) of a crystal was calculated by Debye-Scherrer's formula which is-

$$D=K \lambda/\beta \cos\theta \qquad (1)$$

where 'K' is a nanostructure constant, β is the broadening of the diffraction line of full-width half maximum (FWHM) and λ is the x-ray wavelength about 0.15418 nm.

Fig.2: The Bruker D8 Advance X-Ray Diffraction (XRD).[By Courtesy: Institute Instrumental Centre, IIT Roorkee].

Similarly, other parameters are the lattice strain (ε), dislocation density (δ), the volume of the unit cell (V), and the no. of crystallites per unit area (N) in the crystal lattice is calculated by the following equations.

$$\varepsilon=\beta \cos\theta/4 \qquad (2)$$

$$\delta=1/D^2 \qquad (3)$$

$$V=a^3 \qquad (4)$$

$$N=t/D^3 \qquad (5)$$

where t is the thickness of the thin film.

SURFACE MORPHOLOGY

Surface morphology analysis is done by various techniques such as FESEM, TEM, and AFM, and their detailed information is discussed as follows-

FE-SEM (Field Emission Scanning Electron Microscopy)

FESEM is used for the surface of the sample with remarkably very high magnification. The FESEM is done by Zeiss Ultra-60 as shown in Fig.3, which is used to examine highly magnified images. Mainly, it has three parts. The first part is the scanning part, which includes an electron gun, an optics lens, and various detectors. The third part is a computer for taking images. The scanning beam containing the electron beam is focused on the specimen. Therefore, backscatter electrons (BSE) are captured by the detector and provide the image on the computer screen in various magnifications at various scales. The computer screen provides a magnified image of the sample. The microstructure arrangement of the molecule is used to understand the morphology. Whereas, image j software is used to measure the structure in micrographs. It is only convenient for the conductive surface. For making a sample, surface conductive coating with gold, platinum, and tungsten has been done.

Fig.3: Field emission scanning electron microscopy (FE-SEM) (Zeiss Ultra60). [By Courtesy: Institute Instrumental Centre, IIT Roorkee]

Energy Dispersive X-ray Spectroscopy (EDX)

This gives information about the quantity of elements or contents that are presented in the sample. It is used to scatter back or reflect electrons, whereas X-ray energy converts it into voltage signals. The EDX characterized results provide information about the element present in the sample through a plot between intensity and energy. Each element shows its peak. Therefore, we can say that EDX is used to give information about the element or content that is present in the samples.

Optical Analysis

In the application of nanostructure, optical properties play an important role. It has two branches: UV-Vis spectroscopy of the sample with electromagnetic radiation and the other branch deals with the nature of emission or excitation of photons in the same region, like photoluminescence (PL). The electronic band structure of the same is examined by these characterizations. The detailed study of UV-Vis spectroscopy and PL is studied as follows

UV-Vis Spectroscopy

The UV-Vis 3600 spectrophotometer (Shimadzu Japan) was used to carry out spectroscopic results shown in Fig.4. The range of spectrum was from 185 to 3300 nm and the main components of this instrument are the light source (halogen lamp and deuterium lamp), monochrome tree, mirror, detectors and a software UV probe [12.13]. There were possible transitions from ground to higher molecular orbits by absorbing equal or greater energy of the incident light. The parameters measured by UV spectroscopy are absorbance, transmittance, and reflectance. These optical parameters are the function of incident light wavelength [14]. The other optical parameters were calculated, such as optical bandgap. The optical bandgap is calculated by using a plot between (αhυ)2 vs. hυ named as Tauc plot. The equation can be represented as

$$(\alpha h\upsilon)^{1/n}=A(h\upsilon-Eg) \tag{6}$$

here, ‘A’ is the band edge constant, v is the transition frequency, ‘α’ is the absorption coefficients, ‘h’ is the Planck’s constant where ‘Eg’ is the bandgap energy, exponent n=1/2 for the direct transition, and n=2 for the indirect transition respectively.

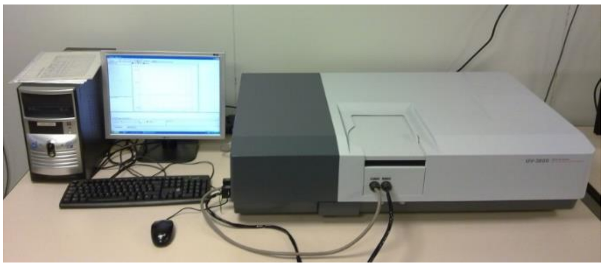

Fig.4: The UV-3600 spectrophotometer (Shimadzu, Japan).[By Courtesy: Semiconductor Research Lab, GKV, Haridwar

Photoluminescence (PL)

The PL has examined the luminescence property of the nanostructure. The He-Cd laser-based system recorded the emission and excitation spectrum of the sample. The light source, monochromators, operating software, detectors, etc. are the main components of the photoluminescence spectrometer shown in Fig.5. The photoluminescence works as the incident light transfers energy to the electron, and the excited electrons reach a higher energy state. This excitation electron, after releasing energy in the form of photons, returns to the initial state. The detector detects the excitation and emission of photons and then these signals are transferred to the CPU. Then, the number of photons results as a function of wavelength. The PL spectrum by the broadening of the peak reveals the wavelength of emission or emitted electrons. The 'PL' spectrum only when emitted electrons are excited to the intermediated band shows the electronic band structure properties, then other peaks appear in the spectrum. The information about defective lattice shows the intermediate peaks.

Fig.5: The Photoluminescence Spectrometer with He-Cd Laser of 325 nm. (By Courtesy: Department of Physics, University of Free State, Bloemfontein, SA)

Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectroscopic spectrum is recorded to understand the molecular configuration, FTIR 8400 S (Shimadzu, Japan) is used, as shown in Fig.6. It works under two main components. The first part is an IR source having a range of 7800-350 cm-1 and the second main component is dexterous (DLATGS) which has a recorded spectrum. The other parts are the beam splitter, and attenuated total reflectance (ATR). As a function of wave number, the FTIR provides a transmittance spectrum of the sample. Every molecule has its signature of the IR spectrum like XRD patterns. The molecule and band structure are identified by comparing them with the standard data.

Fig.6: The FTIR 8400S Fourier transform infrared spectrometer of Shimadzu, Japan. (By Courtesy: Department of Chemistry, GKV Haridwar)

Raman Spectroscopy

Raman spectroscopy is used to analyze the various modes like rotational, vibrational, and other low-frequency modes. A Raman spectrophotometer with a diode laser has been used, as shown in Fig.7. It contains three main components, which are the detector, the monochromatic excitation source, and the optical lens. The diode laser of range 532 nm is used as a light source. Due to weak Raman scattering the detectors are more sensitive. The wide range of wavelengths 200-4000 cm^{-1} A used to record the intensity of scattered lines. Firstly, the Rayleigh scattered photons give a broad peak. Secondly, the stokes and anti-stokes peaks were observed as very weak as compared to the Rayleigh photons. The peak positions of stokes and anti-stokes lines to understand the structure of the sample.

Fig.7: The RIRM–LP Raman spectrometer of RI Instruments & Innovation, India. (By Courtesy: Manufacturing Unit of RI Instruments & Innovation, India)

Electrical Analysis

Electrical analysis plays a very important role in gas sensing applications. The electrical conductivity is divided into DC conductivity and AC conductivity. In DC conductivity, the I-V characteristics are the voltage-dependent electrical property. Whereas AC conductivity is frequency-dependent. The electrical conductivity analysis by DC-electrical analysis is shown in the figure. The system used for analyzing the I-V characteristics is Keithley 4200 SCS USA and the software used is Keithley Interactive Test Environment (KITE), used to demonstrate the DC electrical parameters examined by Keithly as shown in Fig. 8. The resistance is calculated by the following equation

$$\rho=(R.A)/L \quad (\Omega.cm) \qquad (7)$$

where ‘R’ is the load resistance ‘A’ is the cross-section area of the desired thin film and ‘L’ is the distance between the electrodes [15].

Fig.8: The Electrometer SCS-4200 (Kiethley, USA). [By Courtesy: Semiconductor Research Lab, GKV, Haridwar]

The ‘DC’ current density and resistivity of the sample are calculated by two probe I-V measurement that is given by equation-

$$\text{Current density } (J)= I/A \qquad (8)$$

Where ‘A’ is the cross-section area of the film and ‘I’ is the current corresponding to the applied voltage [16,17].

Gas Sensing

Based on properties like photoluminescence, refractive index, and infrared resistivity, different types of gas sensors have been previously reported by researchers [18-23]. Due to easy detection and high sensitivity, resistivity-based gas sensors play an important role. In recent years, various non-toxic gasses like O_2, He, H_2, and Ar gasses for gas sensing properties may attract the researcher’s attention. Gas sensors contain various properties of sensing, like sensor fabrication, gas sensing measurement chamber as shown in Fig. 9, data acquisition unit, and gas concentration measurements. After initializing the above characterization of thin film, the gas-sensing properties were fabricated. On the surface of the thin film, the two silver electrodes were built. The gas sensing application was done by the Gas Sensor Test Rig (GSTR), which contains a stainless steel cylindrical chamber. In the chamber, a sample holder is placed and its temperature is varied from 2 to 200ºC. This temperature is measured by a thermocouple that is placed inside the chamber and is automatically controlled by a computerized thermometer. The target gas flows from the gas cylinder to the chamber through the needle valve. The volume of the test chamber was about 2.6 L. A rotary pump was also used for flushing out the gasses. At first, vacuum 10^{-6} Torr is created, and then introduced target gas.

Fig.9: Gas sensing measurement chamber (By Courtesy: Semiconductor Research Lab, Department of Physics, GKV Haridwar)

The sensor response, response time, and recovery time of the thin film are based on the resistivity variation. The Keithley 4200 SCS was used to detect the electrical measurements of the sensor. A 1V constant DC voltage was applied to the electrodes of the sensor, using Keithley interactive test environment operating software was used to measure the current of the sample. The sample was placed in a chamber of air and measured sensor resistance 'Ra' in the presence of air, whereas after experiencing resistance in air, with the help of a rotary pump, the air is flushed out. The target gas, after attaining a stable resistance, measures the corresponding sensor resistive in gas 'Rg'. Other parameters kept constant, like humidity and other gasses are also kept constant throughout the complete experiments. The sensor response of the sample was calculated by

$$\mathbf{S} = \frac{|\mathrm{Ra}-\mathrm{Rg}|}{\mathrm{Ra}} \qquad (9)$$

where 'Ra' and 'Rg' are resistance in the air and the target gas at pressure 1013 hpa. As the time taken by the sensor reaches 90% of its resistance measured response time by the target gas, whereas the recovery time is measured when the gas is flushed out by the rotary pump from the test chamber and the time taken to reach 10% higher value than initial resistance was measured.

Photocatalytic Degradation

The photocatalytic application is done under visible light irradiation. At first, fixed amounts of the photocatalyst are taken and then mixed in the dye solution. Before experimenting, the required pH was adjusted by HCl and NaOH. The pH factor is an important factor due to the environmental aspects of the photocatalytic reaction [24]. After that, the solution is stirred for some time to mix them well. Take a small dose of this solution of dye/drug. After taking a dose with photocatalyst, the solution is kept stirring in the dark for about half an hour. Again, take a small dose in the dark, then put the solution in sunlight for degradation. After this, the solution was placed in the sunlight for the photocatalytic application. Taking the next dose of it after 15-30 minutes collects the dose to check the degradation rate by UV-spectrophotometer 3600-SCS. The photodegradation efficiency was calculated from the equation-

$$\mathbf{Photodegradationeffeciency}(\%) = \frac{\mathbf{C_0-C_t}}{\mathbf{C_0}}\times\mathbf{100} \qquad (10)$$

Where C0 is the initial concentration for the dye/drug and Ct is the final concentration after time 't'. It demonstrates that the specific surface area as the doping contents increase and enhances the performance of the photocatalytic activity of nanocomposites.

Photocatalyst + hν ⟶ h+ + e- (11)

h+ + dye/drug ⟶ dyes oxidation (12)

Ce3+ + e- ⟶ Ce2+ (13)

Ce2+ + O2 ⟶ O22-(superoxide anion) (14)

O22- + H2O ⟶ Hydrogen Peroxide + O2 (15)

h+ + H2O ⟶ OH- + H+ (hydroxyl radicals) (16)

OH- ⟶ Degradation products (CO2 + H2O) (17)

H2O2 ⟶ Degradation products (CO2 + H2O) (18)

The above equation determines that the surface of the photocatalyst is responsible for the generation of excitons. The free radical OH^-, $H^{+,}$ and superoxide anion O_2^{2-} can degrade the dye molecule in the form of CO_2 and H_2O. Therefore, the electron is injected from the excited dye molecule and a further electron is adsorbed on the catalyst surface in the conduction band of the photocatalyst. An electron trapped by the molecular oxygen present in the photocatalyst generates highly active radicals and is responsible for the photodegradation of dye/drug molecules. Furthermore, the larger surface area of the catalyst leads to greater adsorption and larger degradation. Therefore, a large amount of dye is irradiated by visible light and increases the photocatalytic degradation of the dye/drug.

SCANNING ELECTRON MICROSCOPY (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern [1], [2]. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. Under vacuum, electrons generated by a source are accelerated in a field gradient. The beam passes through Electromagnetic Lenses, focusing on the specimen. As a result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally, the image is displayed on a monitor. In most of the applications, the data collected is over a pre-selected area of the sample surface and following this, a 2D image is generated that shows the various spatial variations. Conventional SEMs with a magnification range of 20X-30000X with a spatial resolution of 50-100 nm can scan areas that vary from 1 cm to 5µm in width. SEMs also can analyze particular points as can be seen during EDX operations which help in determining the chemical composition of the sample concerned.

Fig.10: XRD-Equipment

ENERGY DISPERSIVE X-RAY (EDX)

Energy dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response by hitting the charged particles [1], [2]. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays is focused onto the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron-hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower-energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted. This allows the elemental composition of the specimen to be measured.

TRANSMISSION ELECTRON MICROSCOPE (TEM)

A transmission electron microscope is constituted of (1) two or three condenser lenses to focus the electron beam on the sample, (2) an objective lens to form the diffraction in the back focal plane, and the image of the sample in the image plane, (3) some intermediate lenses to magnify the image or the diffraction pattern on the screen. If the sample is thin (< 200 nm) and constituted of light chemical elements, the image presents a very low contrast when it is focused. To obtain amplitude amplitude-contrasted image, an objective diaphragm is inserted in the back focal plane to select the transmitted beam (and possibly a few diffracted beams): the crystalline parts in Bragg orientation appear dark and the amorphous or not Bragg-oriented parts appear bright. This imaging mode is called bright field mode (BF).In diffraction mode, another intermediate lens is inserted into the image on the screen the diffraction pattern of the back focal plane. If the diffraction is constituted by many diffracting phases, each of them can be differentiated by selecting one of its diffracted beams with the objective diaphragm. To do that, the incident beam must be tilted so that the diffracted beam is put on the objective lens axis to avoid off-axis aberrations. This mode is called dark field mode DF. The BF and DF modes are used for imaging materials to the nanometer scale. SAED and microdiffraction patterns of a crystal permit obtaining the symmetry of its lattice and calculating its interplanar distances (with the Bragg law). This is useful to confirm the identification of a phase after assumptions generally based on the literature of the studied system and chemical analyses.

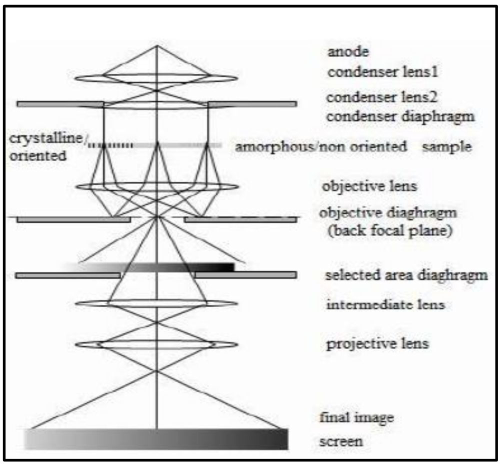

Fig.11.Ray Diagram of TEM

PARTICLE SIZE ANALYSER (PSA)

The technique of PSA is ideally suited for the determination of the size of particles in the nanometer size range. The Malvern Zetasizer Nano Series uses patented optics that provide exceptional levels of sensitivity and allow the determination of the size of samples that contain very small particles and/or particles that are present at very low concentrations [2]. In addition, the backscatter optics allow for the measurement of samples at much higher concentrations than is possible using conventional DLS instruments using a 90° detection angle Particle size is an important parameter for the characterization of nanoparticles. The technique of dynamic light scattering is well suited to the measurement of the size of nanoparticle dispersions. Conventionally, measurement of very small and or poorly scattering particles or samples that are very dilute was difficult unless high-powered lasers were used.

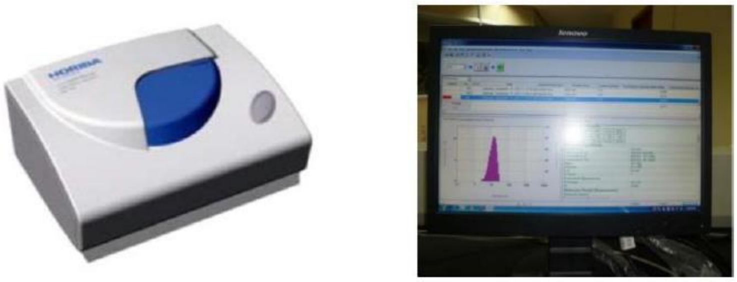

Fig.12.Particle Size Analyzer

ULTRAVIOLET-VISIBLE SPECTROSCOPY

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometer (UV- Vis) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near-ultraviolet (UV) and near-infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. UV-Vis Spectrophotometers are mainly used to measure transmission or absorption in liquids and transparent or opaque solids. It does so by sending a beam of light through the sample and then monitoring the remaining light in a detector. In the case of a UV-Vis spectrophotometer, the light is in the wavelength of 800-200 nm, probing electronic transitions in the sample. It is hard to reach a lower wavelength than 200nm as oxygen starts to absorb light below that wavelength. When the light passes through the sample some of the molecules in the sample will absorb light at various wavelengths of this spectrum, depending on their chemical bonds and structure. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. A spectrophotometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength.

Fig.13: UV-Visible double-beam spectrophotometer

THERMO GRAVIMETRIC ANALYSIS/DIFFERENTIAL THERMAL ANALYZER (TG/DTA)

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique that measures the weight change in a material as a function of temperature and time, in a controlled environment. This is very useful for investigating the thermal stability of a material or to investigate its behavior in different atmospheres (e.g. inert or oxidizing). It is suitable for use with all types of solid materials, including organic or inorganic materials [2]. Differential thermal analysis (DTA) is a calorimetric technique, that records the temperature and heat flow associated with thermal transitions in a material. This enables phase transitions to be determined (e.g. melting point, glass transition temperature, crystallization, etc.). Thermo Gravimetric Analysis (TGA) is a type of testing performed on samples that determines changes in weight concerning temperature changes. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and de-convolution of the overlapping peaks may be required. To determine composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis. Thermal gravimetric analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture and the total mass of impurities liberating upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high-temperature oxidation. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. The thermal analysis and weight loss of the sample are observed by S-II EXSTAR-6000, TG/DTA-6300 thermal analyzer as shown in Fig.14. Simultaneous measurement of these two material properties not only improves productivity but also simplifies the interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g. melting and crystallization) and those that involve a weight loss (e.g. degradation).

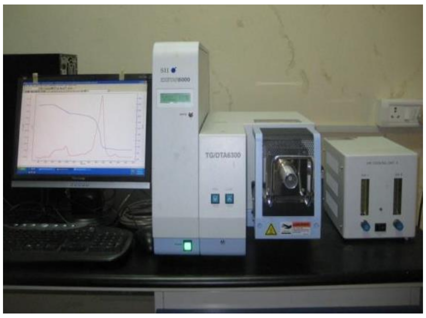

Fig.14.Thermo Gravimetric & Differential Thermal Analyzer.

EXPERIMENTAL DETAILS AND CHARACTERIZATION TECHNIQUES

The metal oxide semiconductor plays a dominant role in various applications. Metal oxide semiconductors like ZnO, CdO, TiO_2, Al_2O_3, etc. have been prepared by various methods like the sol-gel method, magnetron sputtering, the pulsed laser deposition, dip coating and molecular beam epitaxy method, thermal evaporation [1-6]. Among them, the sol-gel method is the most commonly used method to prepare these metal oxide semiconductors. Rare earth doping also plays an important role in various nanocomposites to improve their properties. After preparing these semiconductors, they were characterized by various characterization techniques.

Materials and Methods

Zn, Cd, and Ti have sources like Zinc Acetate Dihydrate [$Zn(COOCH_3)_2.2H_2O$], Cadmium Acetate Dihydrate [$Cd(COOCH_3)_2•2H_2O$], Titanium Tetraisopropoxide (TTIP), respectively. Whereas, the solvent and stabilizers are 2-methoxyethanol, double distilled water, monoethanolamine, and HCL. These chemicals were purchased from Alfa Aesar and Sigma Aldrich companies. The organic dyes were also purchased, like methylene blue and methyl orange. Other reagents like KOH, NaOH, H_2SO_4, NH_4Cl, $MgSO_4.7H_2O$, etc. were also purchased from Sigma Aldrich. The substrates were used as the soda lime glass substrate that was purchased from Shilpa Enterprises in Maharashtra, India. The cleansing agents were used as soap, detergent, HCL, and double distilled water.

Methods: Sol-Gel Method

The synthesis of the metal oxide sol-gel technique is very useful. The Sol-gel method is made up of two terms, 'sol' and 'gel', where 'sol' means colloidal solution and 'gel' refers to a continuously integrated network. The term colloidal is known as the colloidal suspension. Where solid material is permanently suspended in a liquid. Their continuous array forms gels. They are in the form of particles and fibers. Due to these arrays, there should be various dimensions, such as zero, one, two, and three-dimensional. The Sol-gel method has become very helpful for preparing thin film and nanopowder-like samples. This method plays a dominant role in achieving better homogeneity and purity and it plays an effective role in shape, size, and various other properties. The Sol-gel method is used for the fabrication of thin film by a spin coating method, whereas nanopowders were prepared by the precipitation method. A block diagram represents the preparation methods of thin film and nanopowder as represented in below Fig.15.

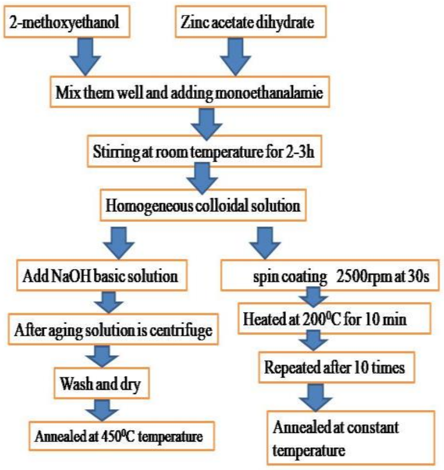

Fig.15: The schematic diagram of the sol-gel process to obtain different nanostructures from precursors

Spin Coating Method

The spin coating method includes thin layers on soda lime glass substrates. This method is used by a machine known as a spin coater, attached to a powerful motor and its maximum spin speed is about 6000 rounds per minute (rpm) and a vacuum pump for the holding substrates as shown in Fig.16. The precursors ZAD (Zinc Acetate Dihydrate) were taken at a certain amount, monoethanolamine is used as a stabilizer.

Fig.16: Spin coater (Metrex Scientific Instruments Private Limit India). (By Courtesy: Semiconductor Research Lab, Department of Physics, GKV Haridwar)

To prepare a better solution of ZnO, first, we take a specific amount of precursor to dissolve it into 2-methoxyethanol or double distilled water. After dissolving it, it is stirred for about 1-2 h to get a desirable solution. Stirring is done by an instrument that is a magnetic stirrer. Thereafter stirring the solution, the desirable amount of solution is then the solution is aged for 12 to 24 h as per the requirements. After aging, the solution is deposited on the glass substrate with the help of a syringe and spun by a spin coater at the rate of 2500 rpm for 30 sec. to prepare a thin film [7,8]. After depositing the thin film, the drying process is as follows. The prepared thin film, after one coating, dried for 10 min. After every 10 minutes, it followed the same steps and then annealed to get the desired thickness of the thin film. The film was annealed at a specific temperature in a microprocessor-controlled furnace to obtain the crystalline nature of the thin film. The sol-gel method is also used for the preparation of nanopowders. The preparation method consists of the precursor 2-methoxyethanol and double distilled water stirred for 2-3 h as required and adding the NaOH solution having a molarity of 1 and pH is nearly 9. After that, the solution is kept for aging and then a desirable paste is left over. The impurities in the solution are removed by ethanol and double distilled water after washing. The drying process was to remove the liquid phase. The temperature for drying is about 100^0C to 200^0C overnight. Then they applied a grinding process to find the fine nanostructured and annealed at the desired temperature to form a crystalline phase. For the phase formation, the annealed temperature plays an important role after annealing of the desired solution observed in the nanopowder samples.

RF Sputtering

For the preparation of thin film, sputtering is one of the physical vapor deposition techniques as shown in Fig. 17. RF sputtering, contains two means of operations, which are d.c. means diode, or triode, whereas the other is a.c. which is radio frequency. It functions in two configurations, which are magnetron d.c. and the other is magnetron a.c. RF sputtering works for both conducting and non-conducting materials. Only when the sputtered material is conducting the d.c. magnetron configuration is operated. If the target is non-conducting, then the positive charge accumulates on the sputtered target, resulting in the sputtering material leading to it going down. The d.c. The magnetron was much faster than a magnetron configuration. The sputtering of the target material is fast, that is 5 to 10 min. So, when the deposition is very fast, the surface of the thin film is not as good as it seems, so fast deposition is not favorable for thin film deposition. Whereas a.c. magnetron configuration for the sputtered material can be both conducting and non-conducting. The rate of deposition of the thin film is very slow. During the thin film deposition, Ar gas is required which interacts with the sputtered materials at the vacuum of nearly 10-6 bar resulting in plasma ambient. By applying the electric field, the energetic-sized particles hit the target and take ions of target materials with them then deposit them on substrates. In the RF configuration, the potential of the target is continuously changed periodically. From plasma, the surface charges are removed by extracting adequate electrons. Whereas for insulating target RF mode works. There are various parameters used, such as the temperature of substrates, water supply, gas pressure sputtering power, etc. In this work, RF sputtering is used for preparing thin film samples; high-purity gasses will be used as sputtering. Whereas the reactive gasses contain titanium metal targets. The sputtering gasses used like Ar/Kr. The total gas pressure will be fixed. The flow rates of both the argon and oxygen gasses will be controlled individually by mass flow controllers. There are two rotator pumps named the rotary pump for 10^{-3} Torr and the diffusion pump for 10^{-6} Torr respectively. Where the vacuum is 10^{-6} mbar in the presence of argon gas and the RF power for the desired thickness will be 110 W.

Fig.17: The Planar Magnetron RF/DC Sputtering Unit Model 12" MSPT (Hind High Vacuum Co. (P) Ltd. Bangalore, India).

CONCLUSION

The basic principles of characterization techniques, such as X-ray diffraction(XRD), SEM, EDX, TEM, DC-Conductivity, Particle Size analyzer (PSA), UV - Visible Spectroscopy, Thermo Gravimetric Analysis/Differential Thermal Analyzer (TG/DTA) are discussed. Nanoparticle characterization parameters include surface area and porosity, solubility, particle size distribution, aggregation, hydrated surface analysis, zeta potential, wettability, adsorption potential, and shape and size of the interactive surface. The heterogeneous/hybrid materials known as nanocomposites are created at the nanometric scale by combining polymers with inorganic solids (such as oxides or clays). It is discovered that their structures are more intricate than those of microcomposites. The characterization of nanomaterials is important for understanding their properties and applications. This review describes the instruments and experimental setups utilized for various measurements towards the characterization of the synthesized nanocrystals. The techniques adopted to characterize the nanoparticles are X-ray diffraction (XRD), SEM, EDX, TEM, DC-Conductivity, Particle Size analyzer (PSA), UV – Visible Spectroscopy, Thermo Gravimetric Analysis/Differential Thermal Analyzer (TG/DTA).

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