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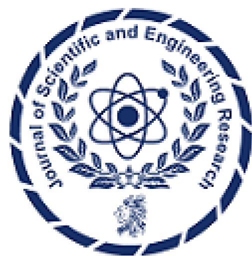

Research Article

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Optical and Chemical Thin Films Characterization Techniques and Recent Important Breakthroughs in Research

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Abstract: An overview of the important Characterization Techniques for Optical Thin Films has been presented. Scientific analysis of the various Thin Films Characterization Techniques like X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass spectrometry (SIMS), Scanning Tunneling Microscope, Transmission Electron Microscope (TEM), Reflection high-energy electron diffraction (RHEED), Atomic force Microscope (AFM), Fourier Transform Infrared (FTIR) Technique, and Differential Interference Contrast Microscope has been given. In addition, some important studies on the topic with technical analysis of results have been briefly presented. Also, a brief discussion of the Material Characterization, Macrostructure, and, Analytical Characterization has been included. Some recent important studies on the scattering loss and the absorption loss of the optical thin films hav been briefly discussed. This overview should be of good utility to the new entrants in the development of high quality optical and chemical Thin Films and their characterization.

Keywords: Optical Spectrometers, X-ray Diffraction (XRD), Electron Microsopy, X-ray Photoelectron Spectroscopy (XPS), Mass Spectrometry, Magnetic Sector Analyzer, SIMS, Atomic Force Microscope (AFM) , and Interference , Spray coating, Sol gel coating.

1. Optical and Chemical Thin Films Characterization

Characterization describes those features of the composition and structures (including defects) of a material that are significant for a particular preparation, and/or study of properties sufficient for the reproduction of the material. A lot of work (1-5) has been done on evolving novel techniques with the capability of providing ever increasing performance. Recent book on Thin Films, Processes and Characterization Techniques (4) describes the creation of new materials thermal evaporation, sputtering, electrochemical and chemical-vacuum deposition; and explains a technology for material evaporation, uniformity calculation, thickness measurement. In addition, this book discusses the correlation of optical and chemical properties obtained from spectroscopic methods. The book provides research scientists and engineers in industry information and data on the materials processing,

characterization, and determination of materials' physical and chemical properties. The book highlights optical and chemical properties obtained on novel materials using a range of deposition methods by two different spectroscopic techniques: SE and UV-VIS-NIR. Emphasizing applications from across a number of domains including Healthcare, Opto-Electronic, and Defence, the book is ideal for academic researchers, graduate/undergraduate students, and practicing engineers concerned with optical and chemical coating technologies. It has now been well established that Thin films of Tin dioxide (SnO_2) are a special class of metal oxides that combine high electrical conductivity with optical transparency since such Transparent Conducing Oxide (TCO) provides an important component for optoelectronic applications (5). Spray pyrolysis deposition for thin film preparation is found to be a simple and relatively cost effective technique. Udayakumar et al (6) have synthesized thin films of tin dioxide using automated spray pyrolysis technique and also have done it's structural characterization. These films were prepared from different concentrations of the precursor solutionand were found to be transparent at low concentration of the precursor solution. They have also presented and discussed the Characterization of these prepared films using X-ray diffraction technique. It has been emphasized that the Spray deposited thin films of tin dioxide have a number of applications, mainly as electrode materials in solar cells.

Material Characterization can be classified into three categories: (i) Microstrutural concerned with morphology, size minor phases, and phase distribution, (ii) Analytical concerned with chemical information and bonding, and (iii) Crystallographic concerned with crystal structure, point group, space group, and orientation. This is done by employing (i) Probe of electron, ion, or photon; (ii) System electronics; and (iii) Response to electron, ion, or photon. The various techniques and instruments employed for this purpose are: Optical Spectrometers, Ellipsometry, X-ray Diffraction, Electron Microscopy, XPS, SIMS, AFM, and Interference. Microscopy is employed to see beyond the sensitivity range and resolution limit of the Eye, and also the Exploration of different wavelength regime (sensitivity) based on Detectors sensitive to different regions of the EM spectrum developed and commercially available, and Enhancement of Resolution Limit of the eye (~1 arc min or 0.35 mm). This is done by using Magnifying Instruments like - Magnifying glass and Optical Microscope (limited by the probe wavelength), Electron Microscope (limited by interaction Volume), and Scanning Probe Microscope (providing atomic resolution). The importance of microscopy can be judged by the fact that the subject has fetched two nobel prizes (1925 for the ultramicroscope with resolution smaller than the wavelength of light, and 1986 for the Electron Microscope with a resolving power of 500A, and also for the STM).

Three major type of Microscopes used are: (i) Optical Microscopes (near field); (ii)

Electron Microscopes - Scanning Electron Microscope (SEM), Transmission Electron Microscope, Scanning Tunneling Electron Microscope (STEM); and (iii) Scanning Probe Microscopes - Atomic Force Microscope (AFM) and Scanning Tunneling Microscope (STM). These techniques are used to study Microstructure and Nanostructure of the films. The common experimental methods for studying Microstructure are: Visual Inspection, X-ray Radiography, and Ultrasonic Inspection. The characteristic features are: Production defects, Porosity, and Cracks. The magnification in this case is unity.: The common experimental methods are: Optical Microscopy, and Scanning Electron Microscopy. The characteristic features are: Grain and Particle Size, and Morphology. The common experimental Methods are: Optical Microscopy, and Scanning Electron Microscopy. The magnification in this case is 100.Microstructure: The common experimental methods are: Scanning and Transmission Electron Microscopy, and Atomic Force Microscopy. The characteristic features are: Dislocation substructures; Grain and Phase boundaries, and Precipitation. The magnification in this case is 10,000. The common experimental methods are: X-ray Diffraction, SPM, and HRTEM. The Characteristic features are: Crystal and Interface atomic structure, Defects, Nano particles and their structures. The magnification in this case is 1,000,000.

The Visible light wavelength is in the range: 4000 - 7000 Å; and the Image formation follows the laws of physical optics, resulting in the Resolution limited by the diffraction limit and wavelength of the light. Electron microscopy makes use of the characteristic of the wave nature of high speed electrons. The electrons accelerated to 10,000 eV have a wavelength of ~ 0.12 Å, and hence the electron microscope provides much higher diffraction limited resolution. The physical nature of a solid surface is studied by the scanning electron microscopy (SEM); and the chemical composition of surface is evaluated by the analytical electron microscopy (AEM). The various characterization techniques for thin films are shown below:

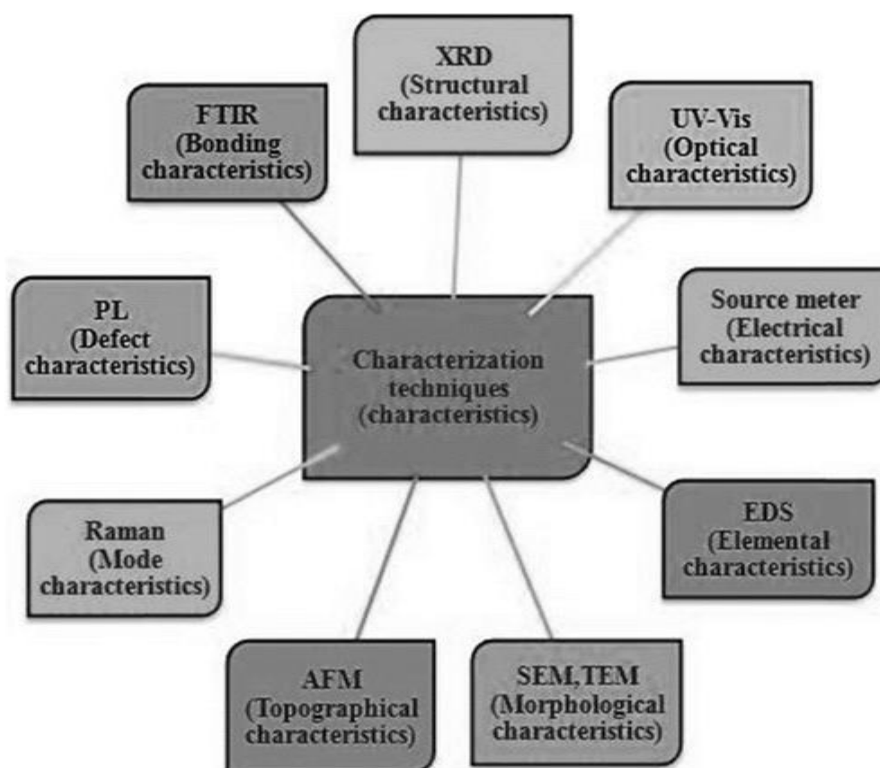

Figure 1: Graphical representation of the various techniques for the characterization of thin films where UV-Vis stands for UV-Visible spectrophotometry and the tools are indicated by their prevalent abbreviations. Figure courtesy Researchgate,net

2. Characterization Techniques

There are many types of Characterization Techniques for studying different aspects of optical thin films. These are based on different concepts, and are technically analyzed below:

(a) Analytical Characterization

Analytical Characterization provides the Chemical Information about the atomic species involved, their distribution, purity, and Bonding Techniques. The Chemical Information and Purity is done by X-ray Analysis - Energy Dispersive X-ray Spectroscopy (EDS) and X-ray fluorescence (XRF). EDS is based on making use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. XRF is based on the emission of characteristic secondary or fluorescent X-rays from a material, which has been excited by bombarding with high-energy X-rays or gamma rays. The Optical Analysis is done by Fourier Transform Infrared (FTIR) Technique; and the related Absorption and Emission spectra. The Bonding is done by X-ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical Analysis. The EDS Line Profile Software automation allows simplified composition profiling at nanometer resolution using EDS e.g. Si80Ge20 islands grown on Si at high temperature ~800ºC followed by Si capping. In the same way, the EDS Mapping allows visualization of the phase separation process, which can be coupled with point-by-point quantitative analysis e.g. Cu50Ag50 ball milled at 230ºC.

(b) X-ray Photoelectron Spectroscopy (XPS):

Photoelectron spectroscopy is based on utilizing photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons, and thereby evaluating the composition and electronic state of the surface region of a sample. With the advent of the development of synchrotron radiation sources, it has become possible to undertake the high resolution studies with radiation spanning a much wider and more complete energy range (95 - 5000+ eV). However, not many studies have been carried out on this topic due to the expensive instrumentation, complexity of the process, and also very limited availability of such sources.

The physical principle involved is simple: The Photoelectron spectroscopy is based on a single photon in/electron out process and the underlying process is comparatively simpler than the Auger process. The

technique uses the monochromatic sources of radiation i.e. photons of fixed energy. The kinetic energy distribution of the emitted photoelectrons, implying the number of emitted photoelectrons as a function of their kinetic energy is measured by using a suitable electron energy analyzer, and thus recording a photoelectron spectrum. This technique has been observed to be necessarily surface sensitive.

The XPS is based on the simple principle: The photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron. Hence, the kinetic energy distribution of the emitted photoelectrons can be measured using any appropriate electron energy analyzer, and thus recording a photoelectron spectrum.

According to theory, for each and every element, there is a characteristic binding energy associated with each core atomic orbital, and therefore, each element gives rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. This implies that the appearance of peaks at particular energies, indicates the presence of a specific element in the sample under study; and the intensity of the peaks is related to the concentration of the element in the sampled region. In this way, the technique provides a quantitative analysis of the surface composition, and so is termed as is Electron Spectroscopy for Chemical Analysis (ESCA).

Commonly used x-ray sources are:

Mg K_α radiation: hν = 1253.6 eV

and

Al K_α radiation: hν = 1486.6 eV.

Therefore, the emitted photoelectrons have kinetic energies in the range of 0 - 1250 eV or 0 - 1480 eV. This technique is necessarily surface sensitive. It is to be noted that when an electron vacancy in the K shell is filled by an electron from the L shell, the characteristic energy/wavelength of the emitted photon is called the K alpha (Kα) spectral line. The intensity vs binding energy of High-resolution X-ray photoelectron spectroscopy (XPS), are shown below:

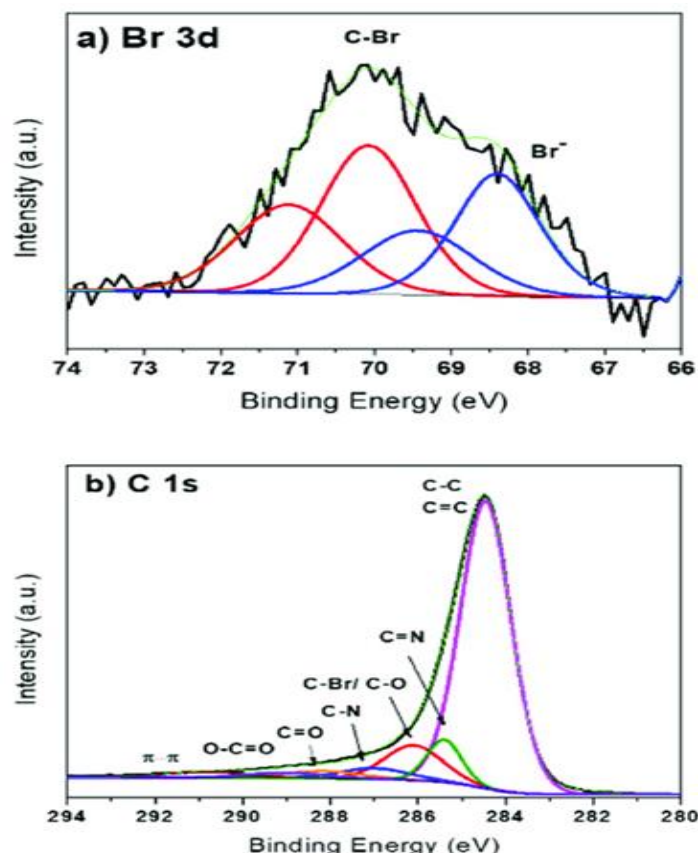

Figure 2: High-resolution X-ray photoelectron spectroscopy (XPS) spectra of Br 3d (a) and C 1s (b). Figure courtesy Researchgate.net

The absorption of the by an atom in a molecule or solid (top), leading to the The absorption of the by an atom in a molecule or solid (top), leading to the ionization and the emission of a core (inner shell) electron (bottom) in XPS and the emission of a core (inner shell) electron (bottom) in XPS is shown below:

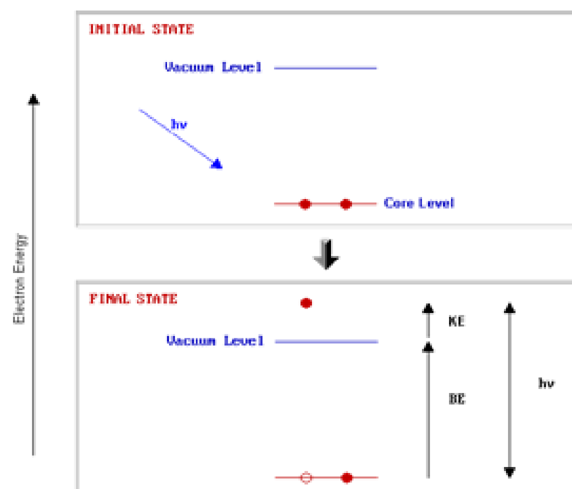

Figure 3: The absorption of the by an atom in a molecule or solid (top), leading to the ionization and the emission of a core (inner shell) electron (bottom) in XPS. Figure courtesy http://www.chem.qmul.ac.uk/surfaces/scc/scat5_3.htm

Obviously, each element gives a characteristic set of peaks in the XPS spectrum. The BE of each peak is specific to the emitting element, and therefore can be used to identify the element. Also, the Intensity of the peak and the area can be used for the quantitative estimation of the element. However, it has to be noted that the exact binding energy of an electron, in addition depends upon: (i) The formal oxidation state of the atom; and (ii) The local chemical and physical environments. Changes in either of these give rise to small shifts in the peak positions in the spectrum, the so-called chemical shifts. XPS measurements have to be done under ultra-high vacuum (< 10- 8 Torr) in order to avoid collision between photoelectrons and gas molecules in the spectrometer, and also to minimize surface contamination from residual gases. X ray photoelectron spectrometer consists of an X-ray source, an electron energy analyzer, and a photoelectron detector, as shown below:

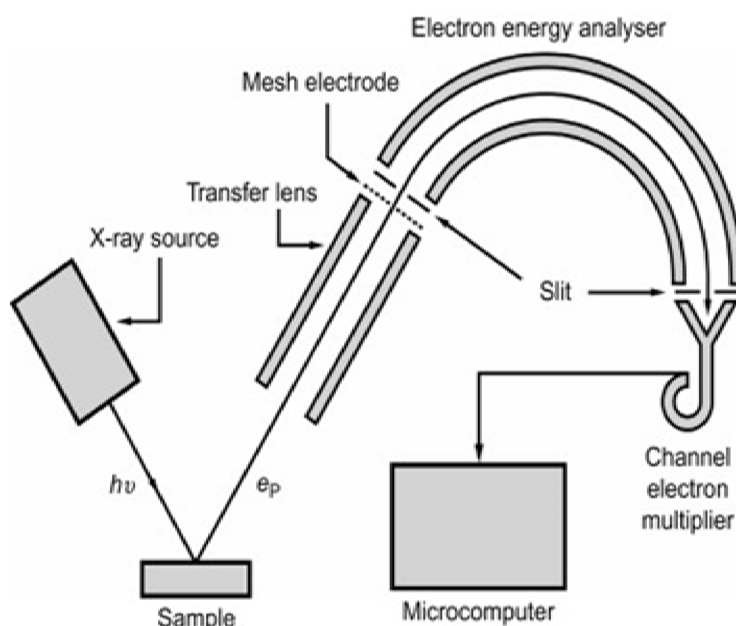

Figure 4: Schematic diagram of an XPS measurement system equipped with an electrostatic hemispherical analyzer (HSA). Figure courtesy Ultralight vacuum, Sciencedirect.com

By using monochromatized X-rays with a narrow line width, satellite spectra exited by Kα3,4 and Kβ lines are eliminated, and the energy resolution of photoelectrons is improved.

(c) Structure by X-ray diffraction

This technique is employed to study the Crystal Structure, by using Bragg's Law, given by:

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

where n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. It is important to note that the moving particles like electrons, protons and neutrons, have an associated De Broglie wavelength.

The various symbols have been explained in the following Figure:

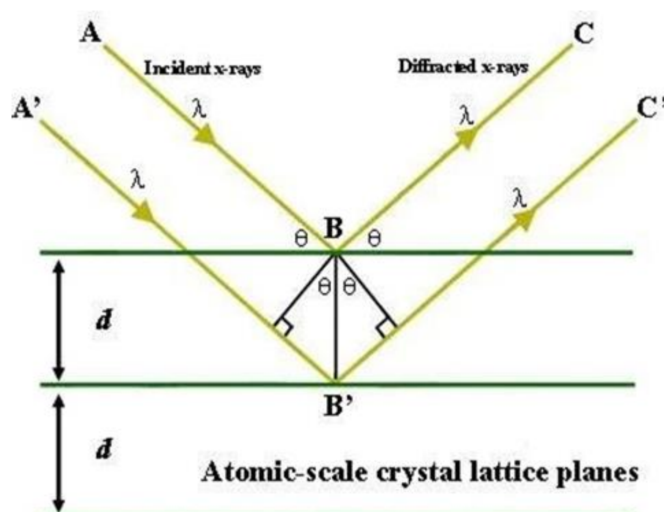

Figure 5: The various symbols used in Bragg's law. Figure courtesy physicsforums.com

(d) Mass Spectrometry

Mass Analyzers are commonly used for Secondary ion mass spectrometry (SIMS), which is the technique used to analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing the ejected secondary ions. This is done by measuring the mass/charge ratios of these secondary ions with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface to a depth of 1 to 2 nm. The Magnetic Sector Analyzers are based on very simple principle: In the magnetic field the ion experiences a centripetal force of, which has to be balanced by the centrifugal force of the ion. The m/e separation is achieved by varying either B (magnetic field) or rm (radius of curvature). The Detector position is kept fixed thereby fixing r, and hence m/e separation is achieved by varying B. The schematic of the Magnetic Sector Analyzer is shown below:

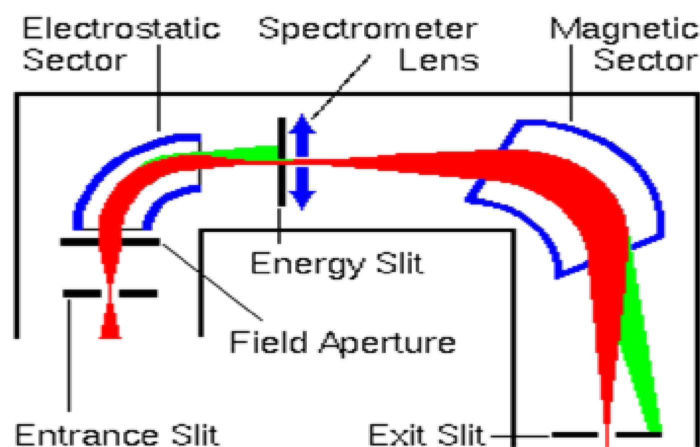

Figure 6: The Magnetic Sector Analyzer. Figure courtesy www.eag.com

As shown in the figure, the modern mass spectrometers have non-normal pole faces for the entrance and exit of the ion beam to the magnetic sector, and the fringing fields in this configuration result in compressing the ion beam in vertical direction, both in and out of the screen, during its passage through the sector. The slits are arranged at the ion beam crossovers for the cleanest separation, meaning the highest mass resolution with similar m/z values. The right part of the beam represents the ions with higher m/z values, which in fact do not pass through the spectrometer. Interestingly, a suitable combination of a magnetic sector and an electrostatic sector provides a double focusing device.

Transmission Electron Microscope

Transmission Electron Microscopy (TEM) is an electron diffraction technique, which samples the bulk of the sample due to the geometry of the system. The TEM images also give very high resolution, and hence are used in studying the structure of optical and chemical thin films

(e) Scanning Tunneling Microscope (STM)

A scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level. For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambient, and at temperatures ranging from near zero Kelvin to a few hundred degrees Celsius.

The STM is based on the concept of quantum tunneling, which explains that when a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them, and the resulting tunneling current is a function of the tip position, applied voltage, and the local density of states (LDOS) of the sample. Information is acquired by monitoring the current as the tip's position scans across the surface and is usually displayed in image form. STM is really a challenging technique, as it requires extremely clean and stable surfaces, sharp tips, excellent vibration control and sophisticated electronics, but is at present commercially available The Schematic of an STM is shown below:

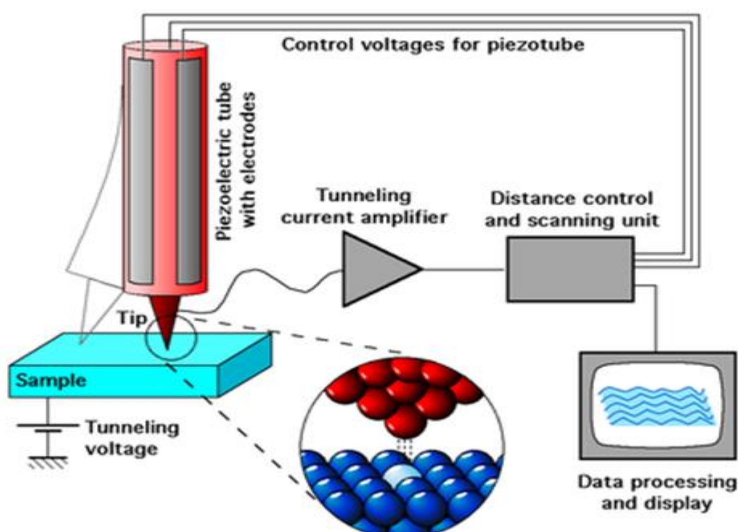

Figure 7: Block Diagram of the Scanning Tunneling Microscope. Figure courtesy www.physicscentral.com

(f) Reflection High-energy Electron Diffraction (RHEED)

RHEED is a technique useful for characterizing the surface of materials. RHEED systems gather information only from the surface layer of the sample, which separates it from other materials characterization techniques that also rely on the diffraction of high-energy electrons. A simple RHEED system requires an electron source (gun), photoluminescent detector screen and a sample with a clean surface. However, the modern RHEED systems have additional parts for optimizing the technique.

The electron gun produces a beam of electrons which strike the sample at a very small angle of incidence on the sample surface. Incident electrons diffract from atoms at the surface of the sample, and a small fraction of the diffracted electrons interfere constructively at specific angles, and hence lead to the formation of the regular patterns on the detector. The electrons interfere according to the position of atoms on the thin film coating on the sample surface, and hence the diffraction pattern at the detector is a function of the coating surface. In this way, the technique is really useful for ensuring the smoothness of the coatings, and hence minimizing the scattering losses. The basic setup of a RHEED system is shown below:

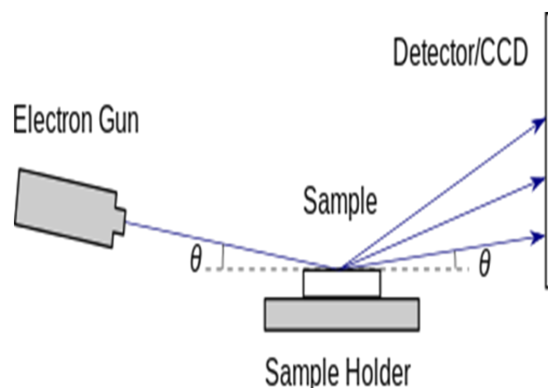

Figure 8: Block Diagram of the Reflection High-energy Electron Diffraction. Figure courtesy en.wikipedia.org

The electrons follow the path indicated by the arrow and approach the sample at angle θ. The diffraction of the electrons takes place from the sample surface, and some of these diffracted electrons reach the detector, and form the RHEED pattern. Also, the reflected beam follows the path from the sample to the detector. Low -energy Electron Diffraction (LEED) is also surface sensitive, but it achieves surface sensitivity through the use of low energy electrons.

(g) Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM), also known or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with resolution ~ fractions of a nanometer, i.e. more than 1000 times better than the optical diffraction limit. The AFM is a very important tool for imaging, measuring, and manipulating thin films at the nanoscale level. Interestingly, the information is obtained by feeling the surface with a mechanical probe.

The principle is simple – The Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command, are used for very precise scanning. Also, in case of the advanced versions, currents can be passed through the tip to probe the electrical conductivity or transport of the underlying surface. However, this is much more challenging and is currently being used by few research groups reporting consistent data. The block diagram of atomic force microscope using beam deflection detection is shown below:

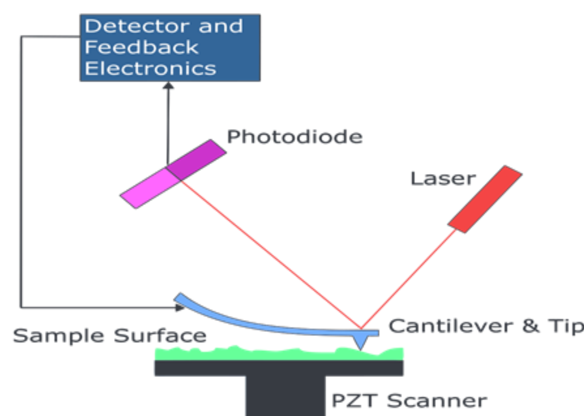

Figure 9: Block Diagram of the Atomic Force Microscope. Figure courtesy en.wikipedia.org

It has to be understood that as the cantilever is displaced because of its interaction with the surface, the reflection of the laser beam is also be displaced on the surface of the photodiode in the same manner.

(h) Fourier Transform Infrared (FTIR) Technique

Fourier transform infrared (FTIR) spectroscopy is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a thin film. Fourier Transform Infra-Red Spectroscopy is a combination of IR absorption spectroscopy and a Michelson interferometer, based on recording the absorption as a function of time, according to the movement of the mirror in one of the interferometer arms. Then, the resulting interferogram is Fourier transformed in to the frequency space to obtain an absorption spectrum. Interestingly, the spectrum is sensitive to the vibrations of the molecular bonds of the sample material.

An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This has a great advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform is required to convert the raw data into the actual spectrum. An FTIR interferogram is shown below:

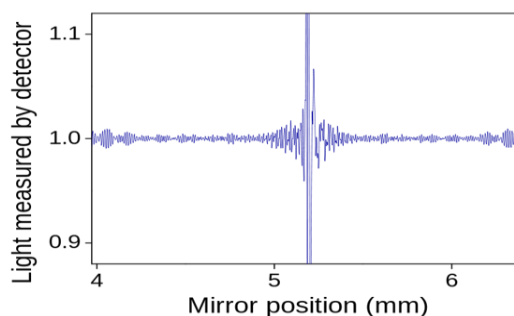

Figure 10: FTIR Interferogram. Figure courtesy en.wikipedia.org

It may be noted that the central peak is at the Zero Path Difference (ZPD) position or the zero retardation where the maximum amount of light passes through the interferometer to the detector. It has to be noted that the interferogram is in the length domain, and the Fourier Transform (FT) inverts the dimension, so the FT of the interferogram is in the reciprocal length domain, i.e. the wavenumber domain. Thus, it is obvious that the spectral resolution (in wavenumbers per cm) is equal to the reciprocal of the maximum retardation in cm.

To have an idea, the calculations show that a 4 cm^{-1} resolution is obtained if the maximum retardation is 0.25 cm, in case of the simple FTIR instruments. Much higher resolution can be obtained by increasing the maximum retardation. The technique is used to find the presence of any unwanted groups (Si-O, OH etc.).

FTIR spectra are also used for studying the effect of annealing at different temperatures of doped thin e.g. ZrO2 -doped TiO2 films. Interesting results are available in the literature, which have been reproduced in the figure given below:

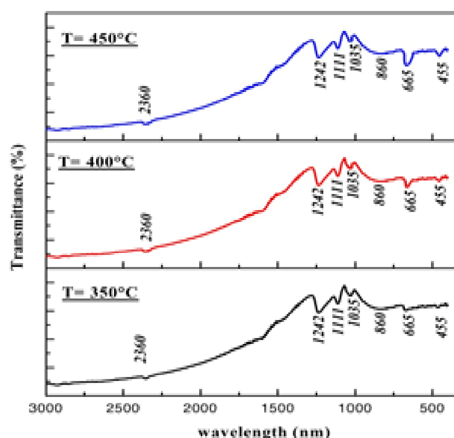

Figure 11: Infrared absorption spectrum of the 5% ZrO_2 -doped TiO_2 films annealed at different temperature. Figure courtesy www.intechopen.com

The figure shows the infrared absorption spectrum of the 5% ZrO_2 -doped TiO_2 films annealed at different temperature. The peak at 2360 cm^{-1} is explained to result from the adsorbed H_2O molecules, which are not removed completely after sol–gel coating. The peaks at 1242 cm^{-1}, 1111 cm^{-1}, 1035 cm^{-1} and 860 cm^{-1} are interpreted to correspond to the vibration mode of Ti-OH. The band around 665 cm^{-1} is especially interesting, and is attributed to the vibration mode of Ti-O-Ti bond, whereas the band around 455 cm^{-1}, is considered to be the O-Ti-O band corresponding to the crystalline titania in the anatase form, which is one of the three mineral forms of titanium dioxide, the other two being brookite and rutile. It is observed that the intensity in vibration bands located in the vicinity of 665 cm^{-1} and 455 cm^{-1} increase on increasing the annealing temperature, which clearly indicates that the number of Ti-O-Ti and O-Ti-O links of titanium dioxide crystallization is also growing.

(i) Differential Interference Contrast (DIC) Microscopy

Differential interference contrast microscopy, also known as Nomarski Interference Contrast (NIC) microscopy or simply as Nomarski microscopy, is indeed an important optical microscopy illumination technique used for enhancing the contrast in unstained, transparent samples. DIC is based on the principle of interferometry to gain information about the optical path length of the sample, and thus to see features, which are otherwise invisible. In this system, a relatively complex lighting scheme produces an image with the object appearing black to white on a grey background, and the image is similar to that obtained by phase contrast microscopy with the added advantage that it is without the bright diffraction halo.

The technique is based on separating a polarized light source into two orthogonally polarized mutually coherent parts which are spatially displaced i.e. sheared at the sample plane and recombined before taking the observation. It has to be understood that the interference of the two parts at recombination is sensitive to their optical path difference (the product of refractive index and geometric path length). By adding an adjustable offset phase, the interference at zero optical path difference in the sample is determined, and this contrast is proportional to the path length gradient along the shear direction, which gives the appearance of a three-dimensional physical relief corresponding to the variation of optical density of the sample, and thus emphases lines and edges, though not providing a topographically accurate image. Thus the technique is extremely useful in studying the scratches and digs in the surface, and hence the microroughness of the uncoated substrates and the coated samples.

The components of the basic differential interference contrast microscope setup are shown below:

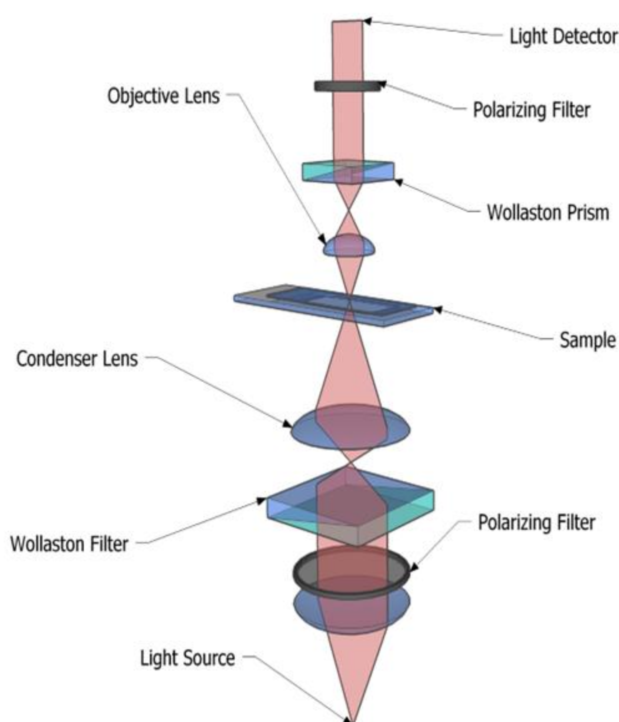

Figure 12: Block Diagram of the Differential Interference Contrast Microscope. Figure courtesy en.wikipedia.org

(j) Ellipsometry

Ellipsometry is based on measuring the change of the polarization of a beam upon reflection or transmission and then using mathematical equations relating the reflection coefficients to polarization. In fact, the technique provides the direct measurement of the complex dielectric constant of the sample, which includes information about the index of refraction and the absorption coefficient. These quantities are dependent on the surface composition, thickness and morphology. The technique is capable of measuring the thicknesses much less than the wavelength of the light used.

3. Some recent important novel breakthroughs and Concluding Remarks on the Scattering loss and the Absorption loss of the Optical Thin Films

With the emphasis on the development of thin films coatings with the improvement in their quality, novel techniques with increased efficiency are being devised, and most of them are even commercially available. For certain applications of Thin Films, the scattering loss (in case of Ring Laser Gyro), and the absorption loss (in case of High Power Lasers) hlave to be minimized for the optimum performance of the Laser systems. In such cases, some of the parameters of the optical thin films like reflectance, scattering and absorption are required to be measured more accurately. The Scatterometer and Photodeflection technique for the absorption measurement are the subjects of interest for the scientists and technologists (7) engaged in the design and development of high quality optical thin films. Schröder et al (8) have presented compact tools like a table-top 3D scatterometer and a CMOS-based scatter sensor and have also reported on the development of a new instrument for spectroscopic angle resolved scatter measurements based on an optical parametric oscillator (OPO) tunable laser, which is a parametric oscillator, that oscillates at optical frequencies. based on converting an input laser wave (called "pump") with frequency ω_p into two output waves of lower frequency (ω_s, ω_i) by means of second-order nonlinear optical interaction, the sum of the output waves' frequencies being equal to the input wave frequency: ($\omega_s + \omega_i = \omega_p$). They have given a new concept, which enhances the capability of photo-thermal absorption measurements with transversal probe beam guiding by overcoming drawbacks such as a lack of sensitivity for materials with low photo-thermal response and/or round substrate geometry. They have introduced the sandwich concept using the laser-induced deflection technique and have tested it for the investigation of highly reflecting (HR) coatings. It has been emphasized that the idea behind the sandwich concept is based on the decoupling of the optical materials for the pump and probe beams. They have realized it by either placing a HR coated rectangular substrate in between two optical (sandwich) plates or attaching a HR coated thin round substrate onto one optical plate. It has been reported that for both configurations, the sandwich concept results in a strong increase in sensitivity for the measurement of HR coatings deposited onto photo-thermally insensitive substrates. Also, the experiments have revealed that for a CaF2 substrate, up to two orders of magnitude enhancement in sensitivity can be achieved. A very good work has been done by Mühlig et al (9), who have described the Enhanced laser-induced deflection measurements for low absorbing highly reflecting mirrors. This work is very useful for research applications. Duo et al (10) have presented a novel technique for characterizing the optical properties of inhomogeneous thin films, that focuses on samples exhibiting absorption in some part of the measured spectral range. Since the conventional methods of measuring the samples only from the film side can be limited by incomplete information at the lower boundary of the film, leading to potentially unreliable results, Duo et al (10) have addressed this issue, by depositing the thin films onto non-absorbing substrates so as to able to do measurements from both sides of the sample. To demonstrate the efficacy of this technique, a combination of variable-angle spectroscopic ellipsometry and spectrophotometry at near-normal incidence was employed to optically characterize three inhomogeneous polymer-like thin subsequently, the spectral dependencies of the optical constants were modeled using the Kramers–Kronig consistent model, which revealed that it is necessary to consider thin, weakly absorbing transition layers between the films and the substrates. Importantly, the obtained results show excellent agreement between the fits and the measured data, providing validation of the structural and dispersion models, as well as the overall characterization procedure. So, it has been emphasized that the proposed approach offers a method for optically characterizing a diverse range of inhomogeneous thin films, providing more reliable results when compared to traditional one-sided measurements.

Hassanien and Sharma (11) have done synthesis, analysis, and characterization of structural and optical properties of thermally evaporated chalcogenide thin novel amorphous thin $Cu_{25-x}(ZnGe)_{25-x}Se_{50+2x}$ (CZGSe)films (0.0≤10.0%) by thermal evaporation deposition technique under the vacuum of ≈ 10^{-4} Pa with almost 500 nm thickness; and have characterized them by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and spectrophotometric transmission measurements. XRD has confirmed the amorphous nature of films, and EDS has proved a fair compatibility between the detected and chosen compositional elements' percentages. Also, the absorption coefficient values have been found to be in the range of 10^4 cm^{-1}. Tauc's bandgap energy, Another important observation made is that E_g increases from 1.456 eV to 1.722 eV, while Urbach's energy, E_e shows a decrease from 0.032 eV to 0.015 eV. Also, the Wemple-DiDomenico and Sellmeier models are applied to study dispersion energies and related parameters. The oscillator resonance energy (E_o) and oscillator dispersion energy (Ed) shows inverse behaviour. The E_o values increase (2.939 eV–3.422 eV), but Ed values show a decrease (30.831 eV–24.342 eV). Many dispersion and nonlinear parameters are also calculated and discussed. of CZGSe films also decreases along all the studied spectral range. They have analyzed correlation between optical parameters of CZGSe films by using Python programming. It has been emphasized that their obtained findings show the possibility of using these films in many optical and research applications.The commercial firms are also making lots of research and development work on developing these instruments.

Najm et al (12) have made an in-depth analysis of nucleation and growth mechanism of CdS thin film synthesized by chemical bath deposition (CBD) technique, with an aim to to acquire a deeper understanding of the response mechanism that is associated with the formation of CdS thin films. They have presented an effective and new hybrid sensitization technique, which involved the 1-step linker between the related chemical bath deposition (CBD) process and the traditional doping method during CBD for synthesizing high-quality, CdS thin films. Also, they have described the mechanism for the combined synthesis of the films. As stated by them,CdS films were electrostatically bonded to soda-lime glass, causing the formation of the intermediate complexes $[Cd(NH3)4]^{2+}$, which aided in the collision of these complexes with a soda-lime glass slide. It is to be noted that in the one-step fabrication technique, 3-Mercaptopropionic Acid (MPA) was employed as a second source of sulphur ions and a linker molecule. Interestingly, their Optical studies showed that the bandgap ranged between (2.26–2.52) eV. CdS + MPA films exhibited a uniform distribution of spherical molecules based on their morphological properties; and especially after annealing, this approach significantly altered the electrical characteristics of CdS films. Whereas the CdS + MPA films displayed the highest carrier concentration, the CdS + Ag + MPA films exhibited the lowest resistivity, with a jump of 3 orders of magnitude. This result is very useful for the designers of Thin Films Characterization devices. Chen et al (13) have given a technique for characterizing the optical properties and thermo-optic effect for non-polar AlGaN thin films using spectroscopic ellipsometry. They have grown non-polar a-plane (1120) AlGaN thin films with various Al compositions successfully on the r-plane (2204) semi-polar sapphire substrates by using the continuous growth, two-way pulsed-flow, and three-way pulsed-flow growth methods, respectively with metal-organic chemical vapor deposition. Subsequently, they have studied the optical properties and thermo-optic effect of these films extensively for the first time with angle- and temperature-dependent spectroscopic ellipsometry (SE) under both isotropic and anisotropic fitting modes. The SE fitting results for the energy band-gap, the layer thickness, and the surface roughness of the non-polar GaN, AlGaN, and AlN thin films have been observed to be to be comparable with the characterization results of high-resolution x-ray diffraction, ultraviolet-visible absorption spectroscopy, and atomic force microscopy. Hence these results revealed that the non-polar AlGaN has higher refractive index than its polar counterpart with the same Al composition, and the non-polar AlGaN with the lowest surface roughness could be achieved with the three-way pulsed-flow growth method. In addition, they have demonstrated that the anisotropy for the non-polar AlGaN thin film increased with increasing the Al composition. Finally, it has been emphasized that these characterization results should be useful for the fabrication of the non-polar AlGaN-based high-temperature power and ultraviolet-polarized optoelectronic devices utilizing thermo-optical effect and optical anisotropy. Their results of Ellipsometric curves displaying angles delta and Psi for various samples have been reproduced below:

Figure 13: Ellipsometry curves displaying angles delta and Psi for 6 samples. Figure courtesy Chen Shuai, Zhang Xiong, Fan Aijie, Chen Hu, Li Cheng, Feng Zhe Chuan, Lyu Jiadong,Zhang Zhe, Guohua Hu1 and Yiping Cui1 Characterization of optical properties and thermo-optic effect for non-polar AlGaN thin films using spectroscopic ellipsometry Journal of Physics D: Applied Physics, Volume 53, Number 20 Citation Shuai Chen et al 2020 J. Phys. D: Appl. Phys. 53 205104 DOI 10.1088/1361-6463/ab77e2. Published 18 March 2020.

It is clear that the curves have widely different shapes; and so the device designer using these films have to consider this post quite well. Khatri and Patel (14) have grown thin films of Copper doped Sulphide (Cu:ZnS slides with a different number of coats varying from 1 to 4 using a low-cost chemical bath deposition technique, and performed the structural, optical, and electrical characterizations with varied film thickness, for investigating their applicability as an alternative to transparent conducting oxides (TCOs). Their X-ray diffraction study revealed cubic phase with sphalerite structure for the films. The effect of thickness on structural parameters as reported in their study, has been reproduced below:

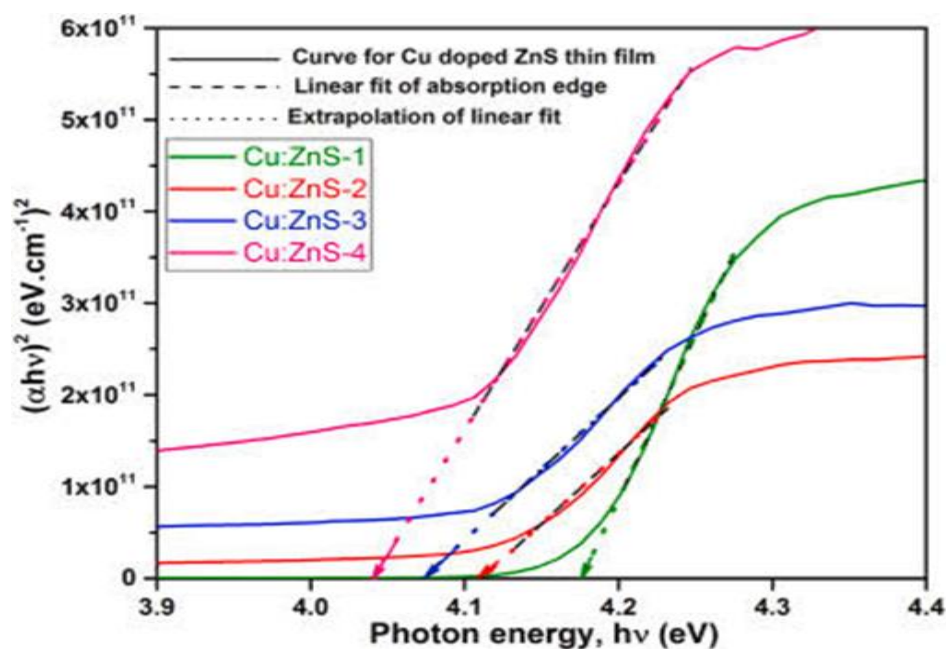

Figure 14: Thickness dependent studies of chemically grown transparent conducting Cu:ZnS thin films. Figure courtesy Khatri Rajeshkumar P. and Patel Amitkumar J., Thickness dependent studies of chemically grown transparent conducting Cu:ZnS thin films for optoelectronic applications, Materials, Volume, October 2021, 111469.

UVV/VIS/NIR spectroscopy demonstrated that transmittance varies from very high value- 98% to average value- 41% in the visible region with film thickness. The increase in film thickness resulted in the narrowing of band gap values. The electrical conductivity between 1.82 and 10.3 $\Omega^{-1}\cdot cm^{-1}$ and charge carrier density in the range of 10^{20} to 10^{22} cm^{-3} were observed in the obtained films. The maximum mobility was 0.185 $cm^2/V.s$. These results show that the Cu:ZnS thin films have a lot of potential to use as transparent conducting sulphide (TCS) film for optoelectronic applications.

Dhruv et al (15) have reviewed the Optical Characterization of Semiconducting Thin Films Using UV-VIS-NIR Spectroscopy, in which he has focused on the growth of thin film and its characterization by UV-Vis-NIR spectroscopy. It is now quite established that for UV-Vis-NIR spectroscopy of thin films, they are usually deposited on translucent quartz glass surfaces. Dhruv et al (15) have reported the extraction of various thin film optical parameters viz., absorption coefficient (α), Urbach energy (Eu), optical band gap (Eg), refractive index (n), extinction coefficient (k), dielectric constants, dissipation factor (tanδ) and optical conductivity (σ optical) by using optical spectra (absorption(A)/transmittance (T)/reflectance (R). Also, they have discussed the effect of thin film substrate temperature (Ts) and/or thickness (d) and/or post-deposition annealing temperature (Ta) on various optical parameters is discussed in detail. Ohlídal et al (16) have studied the Optical characterization of inhomogeneous thin films with randomly rough boundaries exhibiting wide intervals of spatial frequencies. They have presented their results concerning the optical characterization of two inhomogeneous polymer-like thin films deposited by the plasma enhanced chemical vapor deposition onto silicon single crystal substrates. They have determined the Roughness parameters for the rough film and have confirmed the values of the roughness parameters by atomic force microscopy. In addition, they have determined optical constants and thicknesses of both the transition layer. Finally, they have performed a discussion of the achieved results for both the polymer-like films and transition layers. These are results are indeed very useful for research in this field.

Lokesh et al (17) have studied characterization, and prospective optoelectronic applications of DES grafted activated charcoal dispersed polyvinyl alcohol (PVA) films. They have investigated the synthesis, analysis, and utility of films comprising deep eutectic solvent (DES) grafted activated charcoal (AC) within a polyvinyl alcohol (PVA) matrix for optoelectronic device applications. The fabrication process applied by them for this study involves the dispersion of DES functionalization AC into the PVA solution, followed by casting onto

substrates with controlled drying. They have done comprehensive characterization encompassing X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectros-copy, Fourier-transform infrared spectroscopy (FTIR), and impedance spectroscopy which discerns the films microstructure, morphology, conductance, band-gap, and optical traits. In addition, they have discussed the dispersion of DES modified AC in the PVA matrix have converted the insulating PVA to a semiconducting polymeric film with reduced band-gap and increased absorption, which present a propitious avenue for wide array of optoelectronic devices, such as thin film transistors, photovoltaics, LEDs, photodetectors, and many such applications. Their UV-Vis transmittance and reflectances of pure PVA films and TAC-PVA composite films have been reproduced below:

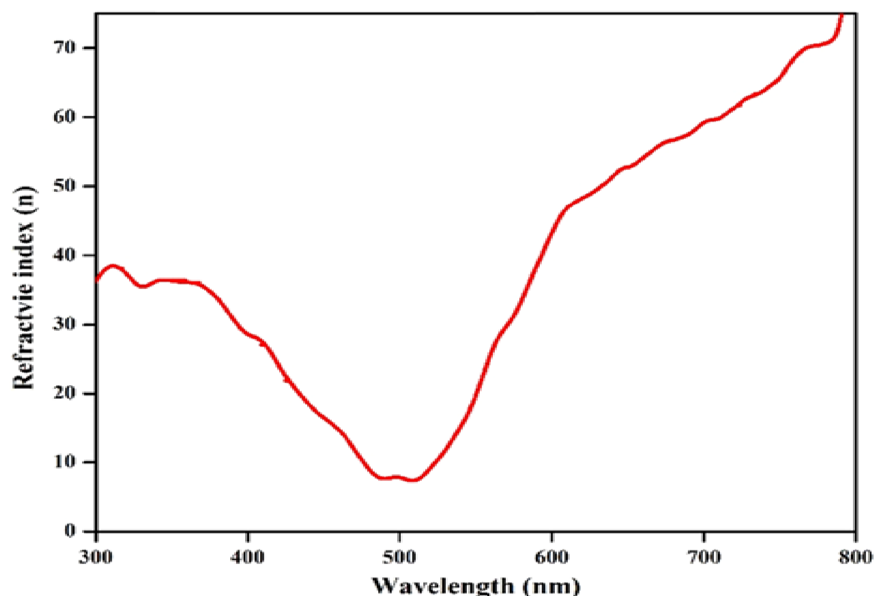

Figure 15: UV-Vis transmittance and reflectances of pure PVA films and TAC-PVA composite films respectively. Figure courtesy Lokesh Kumar S, Binish C J, Rajprasad j Jrp, and Zumaya Tabassum, Synergistic fabrication, characterization, and prospective optoelectronic applications of DES grafted activated charcoal dispersed PVA films, Polymers for Advanced Technologies 35 (5):e6422, May 2024, DOI:10.1002/pat,6422.

As can be seen that A, B illustrates the UV-Vis transmittance and reflectances of pure PVA films and TAC-PVA composite films respectively. The transmittance spectrum of pure PVA films shows a transmittance of 95% above a wavelength of 100 nm. It is observed that upon the incorporation of TAC into the PVA matrix, there is a gradual decrease in transmittance to less than 40%, and this decline in transmittance can be attributed to the interaction between TAC and PVA, which alters the optical properties of the film. Also, it is reported that the uniform dispersion of TAC at various concentrations within the PVA results in higher absorbance, as evidenced in the absorption spectrum. Another important observation is that the decrease in film transmittance is noted as the concentration of TAC increases. These results are very useful in research applications for Optoelectronic devices. It is quite safe to conclude that the subject of the development of more efficient instruments for evaluating the optical thin films is on a firm footing and also evolving fast.

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