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An Overview for Fundamental Chemical Characterization Techniques for Thin Films and Nanostructures

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Today, thin films and nanoscale materials serve as fundamental building blocks for the advancement of technology and technological applications. Understanding and optimizing the performance of these materials relys on chemical and physical characterization techniques. The chemical characteristics of such materials at the atomic and molecular scales is examined through various characterization methods such as X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy, and Raman spectroscopy techniques. These methods provide critical information about the material's characteristics, structural features, and chemical composition. In thin film technologies, the physical and chemical characteristics can affect different parameters of nanostructures such as surface morphology, optical and electrical properties. In nanoscale materials, determining and understanding the chemical structure of the materials plays a crucial role, especially in areas such as catalysis, sensor technologies, and nanoelectronics. These characterization techniques offer essential insights to researchers, engineering and industries which involved in designing, producing, and optimizing the performance of materials at the nano level. For the chemical characterization of thin films, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy, and Raman spectroscopy techniques have been primarily explored for this purpose.

Keywords: *X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared spectroscopy; Raman spectroscopy*

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1. Introduction

Nanostructures are atoms and molecules which come together to form specific structures ranging from a few atoms to several hundred thousand atoms. These structures typically start by the size of a few nanometres and are expected to be smaller than 1 micron. These structures can be categorized into different groups, including zero-dimensional structures (dot structures), one-dimensional structures such as nanotubes and nanowires, two-dimensional structures like nano films, and three-dimensional structures like multilayer films. [1]–[4]. As the dimensions, shapes, or forms of these structures change, significant alterations can be observed in their internal properties. Hence, nanostructures can find applications in various fields, with the most common ones being semiconductor devices, solar cells, sensors, imaging technologies, military technologies, electronic technologies, telecommunications technologies, and biomedical applications [5]–[8]. Nanostructures can exist in various forms, such as nanoparticles, nanorods, nanotubes, nanospheres, and so on. Additionally, they can come together to form thin films [9]. Nanostructures can be found in a powdered form or can be deposited in a liquid. Different production techniques may emerge based on their intended use. Co-precipitation and hydrothermal synthesis are commonly used chemical production techniques. However, these methods are typically employed in the production of nanostructures either in a powdered form or deposited in a liquid. In the production of nano films, vaporization techniques such as thermal vapor deposition or laser vapor deposition and magnetron sputtering techniques, are often preferred [10], [11]. Thin films are material layers in a specific thicknesses, where the structures at the atomic or molecular scale are attempted to be controlled during the production process and such films can be applied to any desired surface [12]. When they are produced for scientific or R&D purposes, thin films are typically grown on a well-characterized substrate with known internal properties. In real-world applications, they are produced by depositing a material layer onto a specific surface. Thin films can have various structural features, arising from different components at the atomic or molecular level [13], [14]. For instance, composite structures derived from specific metals, organic materials and/or a combination of these materials can be utilized to fabricate such films. Thin film characterization techniques enable a comprehensive understanding of various properties such as the physical, chemical, mechanical, tribological, electronic, magnetic properties which are associated with the intrinsic characteristics of materials [13], [14]. One of the key factors determining the properties of thin films is the chemical structure of the atoms and molecules that constituting the films. Thin film characterization techniques allow us to fully understand the physical, chemical, mechanical, tribological, electronic, magnetic, and various other properties of materials. Therefore, the successful application of chemical characterization techniques enables the design of more efficient and more advanced materials through the processing of acquired data. Moreover, optimizing, reducing, or enhancing specific properties of these materials is a crucial step in producing products that meeting the needs of the industry. Progress in these areas contributes to the development of higher-performance and more effective solutions in various fields such as electronic technologies, semiconductor devices, imaging technologies, solar cells, sensors, military technologies, telecommunications technologies, and biomedical applications [10], [15]–[17].

The successful chemical and elemental characterization of nanostructures and thin films at the nanoscale is crucial for understanding and optimizing their properties. For this purpose, methods such as X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX), Raman Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR) are commonly employed.

In our report, we have discussed the techniques which are commonly used for the characterization of nanostructures and thin films such as X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX), Raman Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR). These methods are fundamental methods and are employed to observe changes occurring at various stages of the production process of nanostructures and thin films. Hence, the production process of thin films can be monitored, controlled, and optimized using these techniques.

2. X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique used for surface analysis and chemical component characterization. XPS can perform high-resolution analysis with approximately 10 nm surface thickness on all solid surfaces. The working principle of XPS involves bombarding the sample with monochromatic X-rays, causing the ejection of photoelectrons (electrons bound to energy states), and measuring the energies of these photoelectrons.

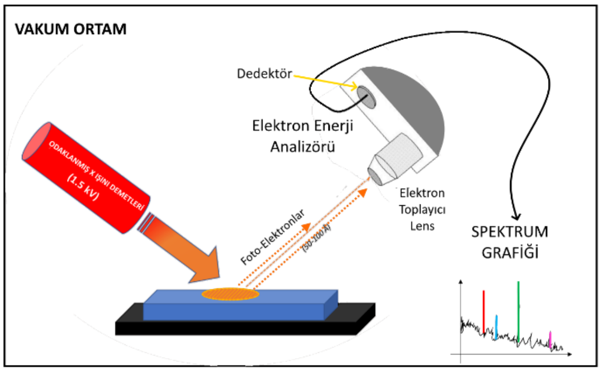

Figure 1: A schematics which illustrate the working mechanism of XPS spectrometer.

In the measurement an X-ray source bombards surface with X-rays energy of which is well defined. The X-rays interact with the atoms on the sample surface, such an interaction cause the ejection of photoelectrons. The kinetic energy of the ejected electrons depends on the energy of the X-rays directed at the sample and the binding energy of the electron. The binding energy is a characteristic value of the atom to which the electron is bound and the orbital it occupies. The electron uses a portion of the energy it receives from the X-rays to overcome the binding energy, leaving the remaining kinetic energy of the electron. The kinetic energies of the photoelectrons are measured using an electron energy analyser, enabling qualitative and quantitative analyses related to the sample.

XPS data can be utilized to determine various parameters related to the sample, such as surface composition, chemical bonds of elements in the sample, surface reactions (oxidation state, etc.), impurities. Moreover, it can also be used to reveal parameters like coating thickness, organization of film thickness, and chemical composition in thin films. The application areas of XPS are quite extensive, widely used in fields such as materials science, surface science, catalysis, nanotechnology, polymers, semiconductors, biomedical applications, and coating industries. For instance, XPS serves as a crucial research tool in monitoring chemical changes in surface modifications where the activity and selectivity of catalyst surfaces can be evaluated. Such implication can be used for the exploration of topics like bio-compatibility and bio-surface interactions.

3. Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-ray Spectroscopy (EDX) is employed for the composition and elemental structure analysis of a samples which covers a wide range of elements from light to heavy. EDX is often used as a side tool of Scanning Electron Microscopy (SEM). Such combination enables researchers to combine elemental analysis with the ability to examine microstructures on the sample, such as surface topography and morphology where a more comprehensive analysis can be conducted. Moreover, elemental information about the imaged surface can be obtained.

In this technique, a high-energy electron beam of electron microscope is directed onto the sample surface and the energies of characteristic X-rays emitted from the sample are collected. Such collected data provide information about the elements which are analysed.

The electron beam striking the sample surface ejects electrons from the sample. If these electrons are removed from the inner (core) orbitals of the atoms, the atoms become unstable. In order to regain stability, high-energy electrons from outer orbits fill the low-energy vacancies in the inner orbits. Such electron displacements release some energy during electron bombardment process. The energy difference between the orbits is emitted as X-rays. The X-rays emitted from material gives characteristic information about the structure and the composition of the material.

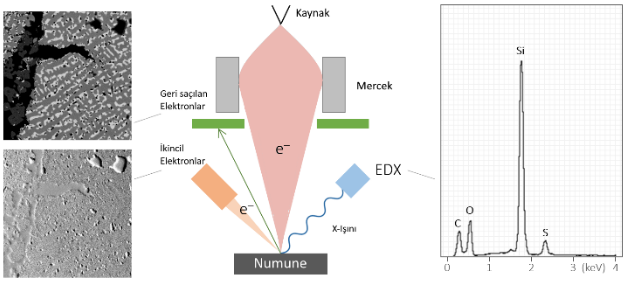

Figure 2: Images obtained from SEM (left side), an illustration demonstrating the working mechanism of EDX (middle) and EDX spectrum (right side)

The application areas of EDX are quite extensive which include materials science, surface science, metallurgy, geology, polymers, biomedical research, and corrosion analysis. Besides, EDX is widely used to determine the distribution of different elements in a sample, detect the presence of inorganic or organic components, assess the quality of coatings, and conduct elemental analyses in material research.

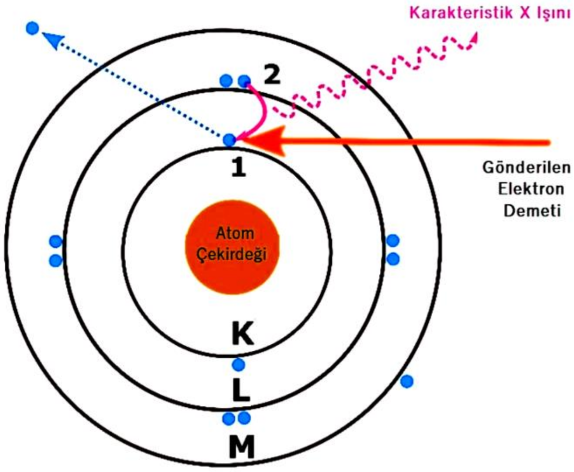

Figure 3: Schematics illustrates X-ray formation after electron bombardment.

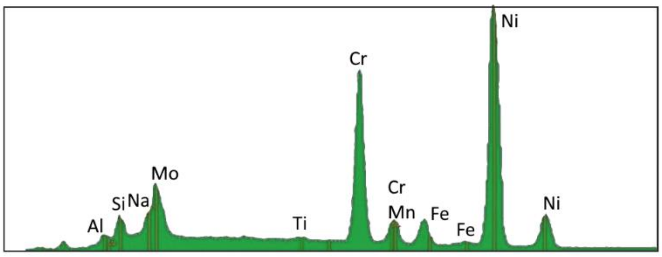

Figure 4: An EDX spectrum. Elemental composition and elemental percentage can be calculated regarding the area below peaks.

4. Raman Spectroscopy

Raman scattering and Rayleigh scattering are two different forms of scattering when electromagnetic light interacts with matter. Rayleigh scattering is an elastic scattering type where light interacts with small-sized particles, and the frequency of the scattered light is the same as the input frequency. The reason for the daytime sky appearing blue and the red color during sunset is due to Rayleigh scattering. Raman scattering is an inelastic scattering type, where photons interact with molecular bonds, and the frequency of the scattered light is different from the input frequency. Raman Spectroscopy is a powerful technique that provides high-resolution molecular analysis. Raman Spectroscopy is used to determine the molecular structures, functional groups, and crystal structures of samples; therefore, Raman

Spectroscopy plays a significant role in the characterization and research of materials.

Raman Spectroscopy detects changes in the energy levels of molecules in a sample by applying monochromatic laser light to the sample. A portion of the incident laser light is scattered, interacting with the vibrational and rotational energies of molecules in the sample to create Raman scattering lines with different energy levels. If the scattered photons provide energy to the vibrational motion (Stokes Raman Scattering), they become lower in energy than the incident light and exhibit an increased wavelength. On contrary, if the scattered photons take energy from the vibrational motion (Anti-Stokes Raman Scattering), they become higher in energy and exhibit a decreased wavelength. The energy difference between the incoming and scattered photons corresponds to the molecular vibrational energy. Each peak in the Raman spectrum is associated with a specific vibration or molecular motion that determines the characteristics of the sample. This spectrum serves as a molecular fingerprint, providing information about chemical bonds.

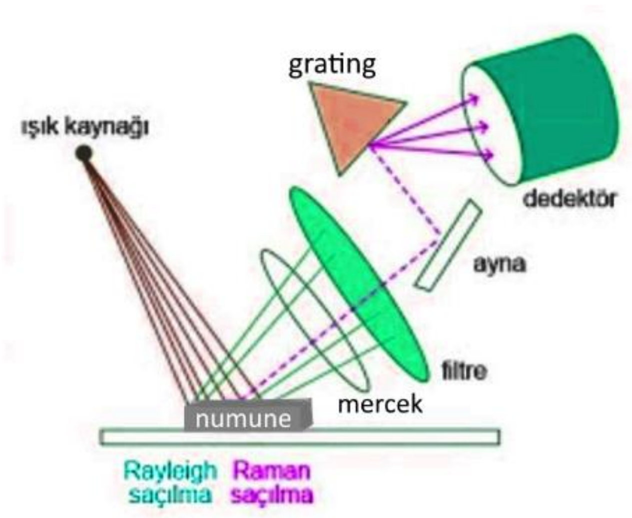

Figure 5: A schematics which illustrate the working mechanism of Raman spectrometer.

The applications of Raman Spectroscopy are broad, and spanning various fields such as chemistry, biomedical research, materials science, pharmaceuticals, food analysis, geology, polymers, semiconductors, and nanotechnology. For example, Raman Spectroscopy is a valuable research tool in fields like biomolecule analysis, drug discovery, material characterization, monitoring chemical reactions, and determining the purity of samples.

5. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a spectroscopic technique. It is often used to analyse the molecular structures, composition, chemical bonds, and functional groups of materials by using their interaction with infrared (IR) light. The FTIR spectrometer operates on the principle of separating infrared light using an interferometer and converting the spectral data through mathematical Fourier transformation. The Michelson interferometer is at the core of FTIR spectroscopy. It consists of two perpendicular mirrors and a beam splitter at the centre. The beam splitter directs half of the infrared light from a source to a fixed mirror and the other half to a moving mirror. The light beams are reflected back to the beam splitter from both mirrors and are recombined at the beam splitter.

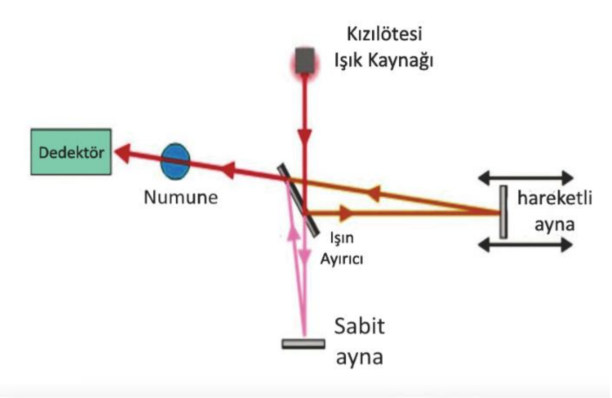

Figure 6: A schematics which illustrate the working mechanism of FTIR spectrometer.

Since one of the mirrors is mobile, the distances taken by two different light beams differ. This optical path difference creates a phase difference between initially identical waves, leading to constructive and destructive interferences between the beams. An interferogram is formed, containing a strong signal at the point corresponding to zero path difference and rapidly decreasing on both sides. Factors such as changes in source intensity and the efficiency of the beam splitter play a role in obtaining the shape of the interferogram when there is no sample. If a sample is present, the combined beam passes through the sample, and the vibrational and rotational motions of the bonds in the sample molecules absorb the light where absorption bands are obtained on the interferogram. The interferogram is detected by a detector and undergoes mathematical Fourier transformation to obtain the FTIR spectrum. This spectrum, displayed via a computer, includes intensity values corresponding to wavelengths and frequencies.

When the optical path difference (OPD) is multiples of the delta wavelength, constructive interference occurs. Specifically, when delta equals the optical path difference, peaks overlap with peaks and troughs overlap with troughs, resulting in constructive interference.

Interpreting the FTIR spectrum requires analysing the absorption bands observed at specific frequencies. These bands assist in determining the presence of functional groups and chemical bond types in the sample. The intensity and position of the bands in the spectrum provide crucial information for identifying the molecular structure and chemical properties of the sample.

FTIR has many advantages. For instance, it is a non-invasive technique, meaning it does not require any physical interaction or destruction of the sample. There are no consumable costs. It provides detailed information about investigated sample. Additionally, it can be applied to various types of samples (solid, liquid, gas). Samples typically require minimal preparation, and the analysis time is quite fast.

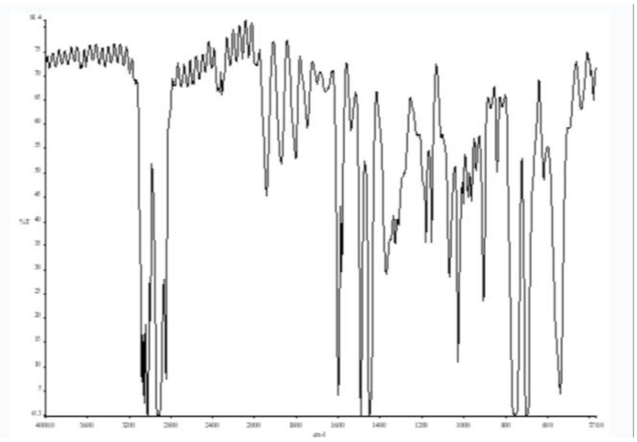

Figure 7: An FTIR Absorbance – wavenumber spectrum

FTIR have quite extensive application areas. It is used in many fields such as chemistry, biomedical research, materials science, the food industry, pharmaceuticals, and polymers. For example, FTIR is a widely used research tool in the analysis of drugs, characterization of biomolecules, and determination of the chemical structure of polymers.

6. Conclusion

The chemical structures play a crucial role in determining the characteristic features of thin films and nanomaterials. In our report, we have discussed fundamental characterization techniques commonly used in chemical analysis and characterizations, such as XPS, EDX, FTIR, and Raman spectroscopy.

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