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X-Ray Photoelectron Spectroscopy Studies of Metal Chalcogenide Thin Films: A Review

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Abstract

X-ray photoelectron spectroscopy (XPS) on sample analysis has the capability to give useful information about the surface layer in thin films. In this work, chemical composition and elemental oxidation states will be studied for binary, ternary and quaternary thin films.

Keywords:* *X-ray photoelectron spectroscopy, Thin films, Deposition, Semi-conductor, Chemical bath, Metal chalcogenide

Introduction

Now-a-days, there are many techniques could be used in order to carry out a full investigation of a surface phenomenon in materials science. For example, transmission electron microscopy [1-5], X-ray diffraction [6-12], scanning electron microscopy [13-16], auger electron spectroscopy [17-19], atomic force microcopy [20-27] as reported by many researchers. Material characterization on a nano or mirco scale is often an essential part for understanding material behavior. Obviously, no one technique can ever solve each surface problem. Therefore, two or more techniques were used by material scientists in their investigation. Some important information such as chemical structure, atomic structure, chemical composition, physical topography, electronic state and description of bonding of molecules will be studied in order to understand the properties of samples.

X-ray photoelectron spectroscopy (XPS) technique has been employed over the past twenty years in many areas of materials analysis include thin films, catalysis, metallurgy, semiconductor, superconductor, biomaterials, chemisorption, polymer, fibre, corrosion and oxidation. In this work, surface properties of thin films were studied by using X-ray photoelectron spectroscopy. The X-ray photoelectron spectroscopy spectra and data were discussed. The advantages of X-ray photoelectron spectroscopy technique will be described as well.

Literature Survey

X-ray photoelectron spectroscopy requires ultra-high vacuum conditions in order to measure photoelectrons emitted from thin films. Generally, X-ray photoelectron spectroscopy spectrum is produced by irradiating a material with a beam of X-rays. X-rays penetrate the specimen surface to a depth of a few micrometers. At the end of the process, the kinetic energy and number of electrons that escape from materials being analyzed.

There are several advantages by using X-ray photoelectron spectroscopy technique. The X-ray photoelectron spectroscopy sensitivity at 0.1 atomic percentage and is used to analyze the surface chemistry of samples. These samples consist of solid form or heavy oil. Generally, X-ray photoelectron spectroscopy detects all elements such as atomic number of 3 and above. Quantitative chemical information of the first 10 nm atomic layers could be done successfully using X-ray photoelectron spectroscopy. On the other hand, X-ray photoelectron spectroscopy is used to provide information on the oxidation state of each element. For instance, X-ray photoelectron spectroscopy can easily distinguish sulphates from sulphites, sulphides or sulphur. Other advantages such as ability to give chemical information, low sample damage, and simple quantitative information.

Chemical composition study by X-ray photoelectron spectroscopy as described by Deshpande et al., 2013 [28] for the CdSe films prepared using chemical bath deposition method at room temperature. The X-ray photoelectron spectroscopy spectra show the strong peaks correspond to Cd 3d, Cd 4d, O 1s and Se 3d. They obtained results are close to that of bulk CdSe. Lisco et al., 2015 [29] have developed pulsed DC magnetron sputtering to sputter cadmium sulphide thin films in highly stable process conditions. The X-ray photoelectron spectroscopy spectra indicate photoelectron core level of Cd 3d and S 2p. The binding energies obtained matched the theoretical values for CdS. They also point out that no oxygen was incorporated into the films and the films are stoichiometric. In the other case, CdS films were prepared using chemical bath deposition method in the presence of tartaric acid as complexing agent as reported by Roy et al., 2006 [30]. X-ray photoelectron spectroscopy analysis supported that the composition of CdS films annealed at 400°C. The peaks positions for Cd 3d 5/2, Cd 3d 3/2 and S 2p were obtained. Zhang et al., 2001 [31] have prepared thin films in alkaline aqueous solution. The X-ray photoelectron spectroscopy results indicate that the contents of Ag and Se are quantified by Ag 3d5/2 and Se 3d peak areas. They comment that the photoelectron emission arising from elements and oxides is not significant. SnS films were synthesized onto tin oxide glass substrates as proposed by Subramanian et al., 2001 [32]. X-ray photoelectron spectroscopy studies reveal that Sn 3d 5/2, 3d 3/2 and S 2p 3/2 peaks were attributed to SnS films. $CuInS_2$ thin films were synthesized by Aggour et al., 2002 [33] using electrochemical deposition. Evaluation of binding energy from X-ray photoelectron spectroscopy shows Cu 2p, In 3d and S 2p peaks attribute to $CuInS_2$ films.

Tin selenide thin films were prepared using electro deposition method as described by Lukinskas et al., 2006 [34]. Determination of elemental composition films was carried out using X-ray photoelectron spectroscopy. They conclude that interchanging deposition of tin and selenium coatings from separate solutions causes formation of SnSe, Se and $SnSe_2$ phases. On the other hand, the chemical composition of CdS films was determined by X-ray photoelectron spectroscopy technique as reported by Urias et al., 2014 [35]. They claim that the annealing treatment has a significant effect on the composition of obtained films. For example, $Cd_{0.6}S_{0.4}$ and $Cd_{0.55}S_{0.45}$ was observed for the as-deposited films and annealed films, respectively. Khot et al., 2014 [36] have synthesized cadmium sulfoselenide thin films using self-organized arrested precipitation method. The X-ray photoelectron spectroscopy data confirmed that the composition of obtained films was a good stoichiometry.

The X-ray photoelectron spectroscopy technique was employed to investigate elemental oxidation states for samples. Cu-Fe-Sn-S thin films were prepared by Meng et al., 2015 [37] using magnetron sputtering method. They reveal that the Cu^{+}, Fe^{2+}, Sn^{4+} and S^{2-} in the prepared films. Kamble et al., 2016 [38] have prepared $Zn_xCo_{1-x}S$ films via chemical deposition method in an aqueous alkaline. The X-ray photoelectron spectroscopy studies established chemical states of Co^{2+}, Zn^{2+} and S^{2-}. Reddy et al., 2015 [39] have reported the deposition of Cu_2SnS_3 films on soda lime glass by using co-evaporation deposition techniques. X-ray photoelectron spectroscopy analysis reveals that the oxidation states of Cu^{+1}, Sn^{4+} and S^{-2}.

However, there are some limitations of technique such as sample compatibility with ultra-high violet and relatively poor lateral resolution of the x-ray source. In terms of elemental analysis, X-ray photoelectron spectroscopy is unable to study the helium and hydrogen due to these elements have not core orbitals. I believe that the technical aspects of X-ray photoelectron spectroscopy will be improved and the number of areas of application has also grown considerably in future. As a result, making X-ray photoelectron spectroscopy technique almost mandatory in materials sciences as reported by many researchers in their research findings [40-50].

Conclusion

Chemical composition and elemental oxidation states were investigated by using X-ray photoelectron spectroscopy. Evaluation of binding energy from X-ray photoelectron spectroscopy shows the complete synthesis for the desired binary, ternary and quaternary thin films.

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