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Transmission electron microscopy studies on chalcogenide thin films

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ABSTRACT

Transmission electron microscopy technique has a wide range of applications as reported by many researchers. Generally, transmission electron microscopy images are detailed and able to produce information of surface features, shape, size and structure. In this work, transmission electron microscopy was used to investigate the formation of thin films by using different deposition methods.

Keywords: transmission electron microscopy, thin films, grain size, deposition.

INTRODUCTION

Preparation and characterization of chalcogenide thin films are so important in scientific world. Scanning electron microscopy [1-12], transmission electron microscopy, atomic force microscopy [13-26] and X-ray diffraction techniques [27-39] have been used to study the properties of films as reported by many researchers.

Transmission electron microscopy (TEM) is an important technique for a number of various research areas such as nanotechnology, material science, engineering, medical and forensic analysis. Generally,it could be used to explore the micro and the nano world as reported by many scientists. There are many useful results such as topography, morphology, composition and crystalline information could be obtained by using transmission electron microscopy. Briefly, it comprises a variety of methods including dark field, bright field, electron diffraction and high resolution transmission electron microcopy. During an investigation, it employs a high energy electron beam transmitted through a very thin sample to image and analyze the structure of materials.

In this work, a brief review on the characterization of thin films using transmission electron microscopy was discussed. Thin films have great potential for applications in semiconductor, solar cell and optoelectronic devices. Transmission electron microscopy has many advantages including high quality of images could be captured, it is easy to operate with proper training, it offers the most powerful magnification and greater resolution. Therefore, it has attracted great interest among researchers to investigate the properties of various types on thin films including binary, ternary and quaternary chalcogenide thin films.

Literature survey:
In this work, the grain growth of various thin films produced using different deposition techniques was studied using transmission electron microscopy (TEM). The CdS films grown by thermal evaporation at various substrate temperatures such as 20 °C, 100 °C and 200 °C as pointed out by Jassim et al., 2013 [40]. The TEM images indicate a uniform and homogeneous surface with well-defined grain boundaries. Furthermore, they claim that no cluster formation could be seen. Finally, it can be seen that when the substrate temperature increases, the grain size values of CdS are reduced from 42 nm and 36 nm.

The studies of the properties of ZnS films prepared using modified chemical bath deposition method have been done using TEM as described by Lee et al., 2008 [41]. The control of particle size is needed in order to prepare high quality of films for better devices and applications. In their experiment, the observed particle size from TEM analysis was about 5 nm. TEM results proposethat the films have a predominantly zinc blend phase, with diffraction peaks from (111), (220) and (311) planes.

Sometimes, the structural analysis was studied with TEM in order to confirm the exact structure of the films. The CdS films were deposited on fluorine doped tin oxide coated glass substrates using pulsed direct current magnetron sputtering. The TEM back scatter diffraction map reveals that sputtered grains have a high level of texture in the (111) plane and indicate the hexagonal phase, consistent with the XRD patterns as suggested by Lisco et al., 2015 [42]. Additionally, the TEM results highlighted the columnar structure of grains and the grain size was about 50 nm.

In other case, CdS films were prepared by chemical bath deposition technique from aqueous solutions of $CdCl_2$ and $CS(NH_2)_2$ as proposed by Li et al., 2005 [43]. It is well known that cadmium sulphide films form two major phases, namely cubic and hexagonal phase. In their works, the hexagonal CdS films with (002) direction were successfully produced for the first time in the presence of wetting agent such as polyglycol. They notice that all the obtained (*hkl*) indices of the diffracted rings matched well with those of the Joint Committee on Powder Diffraction Standards data for hexagonal CdS. Furthermore, a preferential columnar growth parallel to the substrate edge was recognized as shown in TEM studies. Lastly, hexagonal CdS films were preferable for solar cell application because of excellent stability compared to cubic phase.

Cathodic electrodeposition of CdSe films on fluorine doped SnO_2 coated glass substrates was carried out at 120 °C by Datta et al., 2006 [44]. Microstructure of the obtained films was investigated using TEM. The TEM images confirm the polycrystalline nature of the deposits and compactness of the different micro crystallites in the interior portion of the film matrix.

Yoshifumi & Karen, 2014 [45] have reported the thermal evaporation and characterization study of ZnS film using TEM technique. The average crystallite size ranged from 1.6 nm to 2.5 nm as shown in TEM image of ZnS films deposited by sputtering process.

TEM is considered as important tool to determine crystal size and its distribution as pointed out by Kale &Lokhande, 2005 [46]. They have synthesized CdSe films at room temperature using chemical bath deposition method. The "as-deposited" films were red in colour. The crystallite size was about 4 nm as shown in TEM image. Furthermore, some of the amorphous matrix is significantly observed around some of the CdSe crystals. In other words, CdSe films consist of both nanocrystalline and amorphous phases with same stoichiometry. On the other hand, Zhang et al.,2000[47] selected an alkaline selenium solution as a selenium source in order to prepare CdSe films at room temperature under atmospheric pressure. The obtained films are spherical, slightly agglomerated and the sizes ranging from 4-7 nm. Additionally, the reflections of planes such as (111), (220), and (311) of cubic phase of CdSe are clearly seen as indicated in TEM analysis.

Electron beam irradiation method has been developed by Li et al., 2008 [48] to prepare PbSe films under 350 kGy irradiation dose. It could be seen that the particles were homogeneous, spherical with the size ranged from 20-40 nm. They express that the TEM is able to yield information of surface features, shape and size. Also, they declare that the TEM results were in good agreement with XRD data. In other words, the films show reflections along (200), (220) and (331) planes corresponding to formation of cubic structure of PbSe.

Lokhande et al., 1998 [49] presented the results of ZnSe films prepared by decomposition of selenourea in an alkaline solution. It is well-known that the deposition of zinc selenide films is based on the slow release of zinc ions and selenide ions in a solution which then condense onto the substrate. The cubic ZnSe could be confirmed and crystal sizes are found to be 20 to 25 Å as shown in TEM results. Furthermore, the structural features fit into cubic with typical lattice spacing of 3.2 Å could be identified also.

TEM has been employed to identify the structure of $CuInS_2$ films as supposed by Khan et al., 2012 [50]. These films were produced using spray pyrolysis method at 300 °C. They recommend that the grain size is on a nanometer scale (15 nm) and their surface is smooth. Also, they point out that the lattice plane spacing about 0.31 nm corresponding to (112) plane of tetragonal structure of $CuInS_2$.

The benefit of TEM such as it could be used to confirm the existence of only the chalcopyrite phase of $CuInSe_2$ as announced by Chraibi et al., 2004 [51]. In their experiment, they found that the identification by the XRD is made difficult by the overlapping of the peaks corresponding to the various phases. According to their observation, bad crystallinity can be established for the films prepared before annealing process.Analysis from the TEM images reveal that the mixture of Cu_2Se, CuSe and $CuInSe_2$ phases for the films prepared at the potential of -0.62 V versus

Ag/AgCl. However, only the chalcopyrite phase of $CuInSe_2$ could be created at the potential of -0.57V versus Ag/AgCl. In this case, TEM provides information on compound structure.

Pani& Singh, 2013 [52] have fabricated Cu_2ZnSnS_4 films on molybdenum coated glass substrates by Doctor's Blade technique. From the TEM study, particle size is below 10 nm and agglomerated. Wang et al., 2013 [53] have addressed the preparation of Cu_2ZnSnS_4(CZTS) films using RF magnetron sputtering method. Higher substrate temperature such as 250 °C produced a flower like structure with assize about 500 nm as shown in TEM image. Also, the selected area electron diffraction pattern could be assigned to (112), (103), (220) and (312) planes. CZTS films have been constructed using solution based deposition method on soda lime glass by Xia et al., 2013 [54]. The as-synthesized films were characterized using TEM. It was clearly seen that the nanocrystals are slightly polydispersed and the size was 10-20 nm. Also, the TEM image demonstrates the interplanar spacing of the (112) to be 3.1 Å.

Lead sulphide thin films have been prepared using chemical bath deposition method in the presence of $Pb(COOH)_2$ and $SC(NH_2)_2$. The obtained films were gray black in color and good adhesion to the substrateas observed by Rene et al., 2013 [55]. TEM analysis exposes that thin films are homogeneous surface and have small crystal (20-30 nm) in the form of spheres. Furthermore, good crystallinity could be supported from the obtained results such as the lattice fringes extend to the edges of the particles.

There are several disadvantages of transmission electron microscopy could be identified many researchers. Generally, transmission electron microscopy is more expensive than scanning electron microscopy. Additionally, it has relatively high maintenance and repair costs. On the other hand, technician must attend a series of trainings before can operate it. Because of technician must know how to handle and manage it in proper way. During analysis process, it requires that specimens be put inside a vacuum chamber. Lastly, it only can produce two dimensional images, black and whitein colour if compared to atomic force microscopy.

CONCLUSION

Transmission electron microscope is the most powerful microscope technique to produce high resolution, two dimensional images at a maximum potential magnification of 1 nanometer. The obtained results indicated that transmission electron microscope could be used in order to investigate the properties of thin films. Transmission electron microscope images successfully provide topographical, morphological and crystalline information.

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