Chapter four

4.0 Experimental work

4.1 Introduction

This chapter described briefly the method which is used for preparing manganese sulfide thin films samples; in this study physical evaporation method was used to grow the MnS thin films on glass substrate, it also described the equipment used and the data collected.

It also speaks about the experimental procedures used to investigate the optical properties of MnS thin films. A tantalum boat was used as support to evaporate MnS.

4.2 Apparatus and experiment procedures:

Thin films which utilized in this research were prepared by Physical vapor deposition (PVD), by using the coating unit (model19E/196 Edwards high vacuum). The optical properties characterization is made by using the Ultraviolet-visible spectrometer, A Michelson Interferometer model No.GlG5002, serial 3495 was used.

4.2.1 Manganese Sulfide:

Manganese is an element found in nature. Pure manganese is a silver metal that has no special smell or taste. Pure manganese combines with other elements to form different manganese compounds. Manganese is an essential (needed) nutrient that plays an important role in our health. The Manganese Sulfide used in this experimental was bought from Chemistry Department, University of Khartoum. Manganese sulfide is a chemical compound of manganese and sulfur.

4.2.2 Synthesis:

Manganese sulfide can be prepared by reaction of manganese salt (such as manganese (II) chloride) with ammonium sulfide:

$$(NH_4)_2S + MnCl_2 \longrightarrow 2\ NH_4Cl + MnS \quad (4.1)$$

4.2.3 Physical and Chemical properties

Information regarding the physical and chemical properties of manganese is located in the table below.

Table No 4.1 some characteristic of MnS:

Characteristic	Information
Trade name	Manganese sulfide
Molecular weight	87
Synonyms	Manganese (II) sulfide
Chemical family	Metal sulfide
Molecular formula	MnS
Physical states	Solid
Melting point	700C°
Appearance and odor	.Pink-green or brown powder

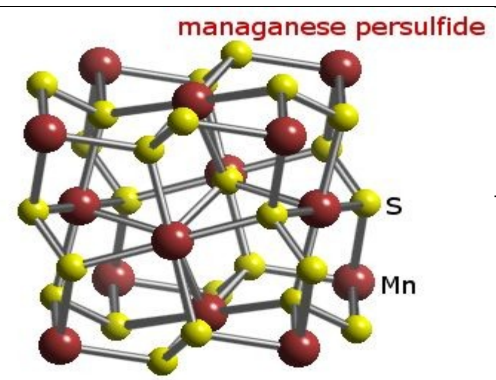


Figure 4.1 Manganese Sulfide crystal structure.

Manganese sulfide, MnS is a wide band gap around (Eg) 3.0 eV semiconductor with potential interest in short-wavelength and belongs to semiconductor materials [50, 51].

MnS used in solar cell applications, prepared at low temperature. The γ-phase of MnS can be prepared at low temperature, but they turned to α-phase above $200C^0$. The α-phase is retained at all temperatures [52, 53, and 54].

4.2.4 Acetone:

It's used for cleaning glass substrate, distilled water used as solvent.

4.2.5 Syringe:

Syringe used to inject the samples of thin film on substrates.

4.2.6 Electrical Furnace:

Used for treatment samples at different temperature and times.

4.2.7 Laser source:

Laser source type (He-Ne) drive model (11341006-1013738) with wave length 632 nm was used to measurement the thickness and optical properties of deposited MnS thin film layer.

4.2.8 Thermal evaporation coating unit:

The thermal evaporation (coating unit model 19E/196) Edwards High Vacuum used for deposition of Manganese Sulfide thin films. The requirements for the vacuum evaporation are sufficiently low threshold pressure, and working champers uncontaminated by organic vapors. These two requirements necessitate the use of high vacuum pumps with sufficient pumping speeds and the shortest and widest possible connecting tubing between the pump and the exhausted space.

Figure 4.2 thermal evaporation deposition system (Coating units).

4.2.9 Michelson interferometer:

Michelson interferometer consists of a source of light, two mirrors and beam slitter. A (He-Ne) laser holder, screen, and Vernier were also used. The Michelson interferometer is a device that produces interference between two beams of light. A diagram of the apparatus is shown in Figure 4.1 the basic operation of the interferometer is as follows. Light from a light source is split into two parts. One part of the light travels a different path length than the other. After traversing these different path lengths, the two parts of the light are brought together to interfere with each other. The interference pattern can be seen on a screen. Light from the source strikes the beam splitter (designated by S). The beam splitter allows 50% of the radiation to be transmitted to the translatable mirror M1. The other 50% of the radiation is reflected to the fixed mirror M2. The compensator plate C is introduced along this path to make each path have the same optical path length when M1 and M2 are the same distance from the beam splitter. After returning from M1, 50% of the light is reflected toward the frosted glass screen. Likewise, 50% of the light returning from M2 is transmitted to the glass screen. At the screen, the two beams are superposed and one can observe the interference between them.

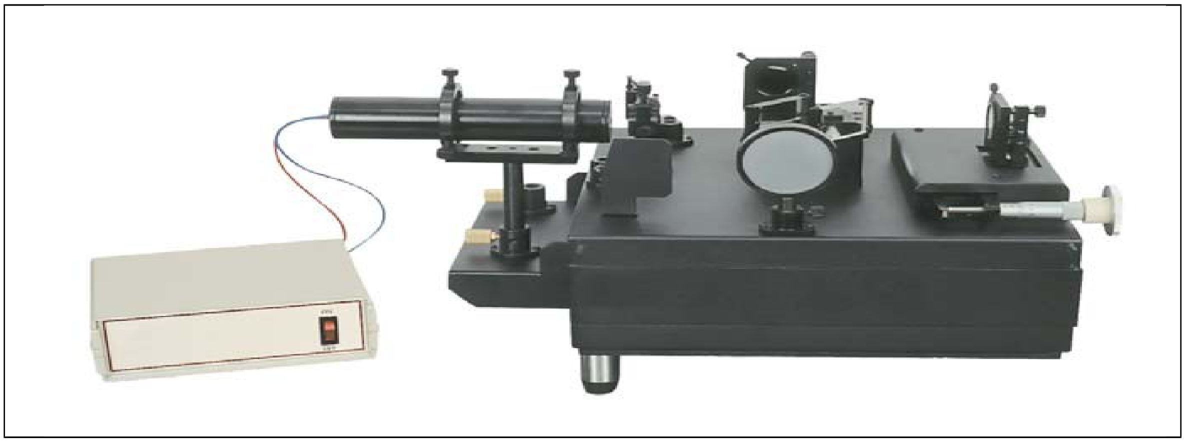


Figure 4.3 Schematic view of Michelson interferometer

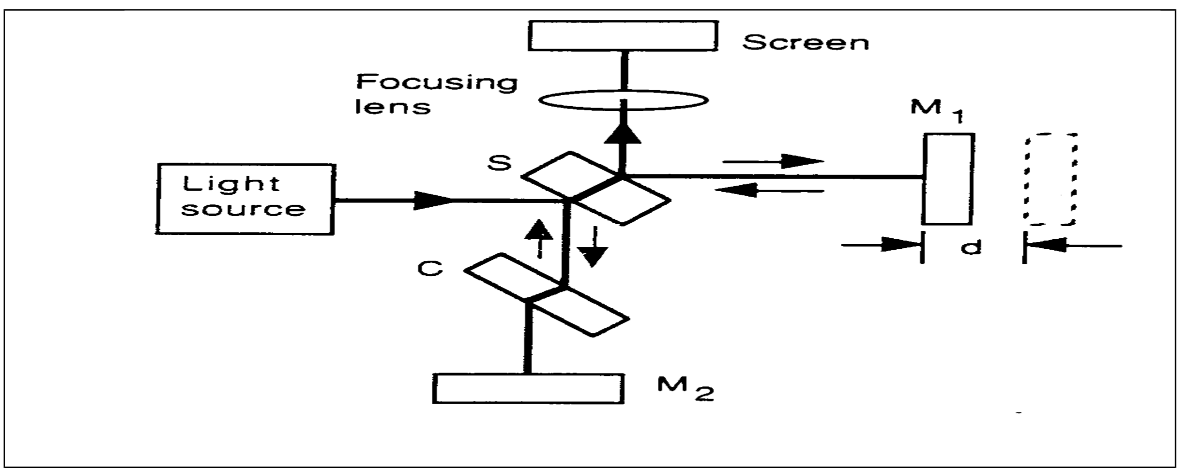


Figure 4.3 Schematic illustration of a Michelson interferometer.

4.2.10 The Ultraviolet-visible spectrometer:

The UV-Visible spectra obtained in Shimadzo mini 1240 spectrophotometer used for analysis of samples for optical properties and scanning between(190-800)nm. The spectrophotometer measures how much of the light is absorbed by the sample. The intensity of light before going into a certain sample is symbolized by I_o. The intensity of light remaining after it has gone through the sample is symbolized by I. the fraction of light transmitted is (I/I_0), which is usually expressed as a percent transmittance (T%), light source it is 20 W halogen lamp (Long life 2000 hour), from this information, the absorbance of the sample is determined for that wavelength or as a function for arrange of wavelengths. Sophisticated UV/Vis Spectrophotometers often do this automatically.

Although the samples could be solid (or even gaseous), they are usually liquid. A transparent cell, often called acuvette, is used to hold a liquid sample in the spectrophotometer. The path length L, through the sample is then width of the cell through which the light passes through. Simple (economic) spectrophotometers may use cuvettes shaped like cylindrical test tubes, but more sophisticated one use rectangular cuvettes commenly1cm in width. For just visible spectroscopy, ordinary glass cuvettes may be used, but ultraviolet spectroscopy requires special cuvettes made of a UV transparent material such as quartz [48].

An ultraviolet-visible spectrum is essentially a graph of light absorbance vs. wavelength in arrange in arrange of ultraviolet or visible regions. The changes in absorption against wave lengths are plated as in figure (4.3) and produce an absorption spectrum.

Figure 4.4 UV- visible spectrometer

4.3 Structural measurements:

The structural characteristic of MnS samples investigated by using differential thermal analysis (DTA) techniques.

4.3.1 Differential thermal analysis (DTA) techniques.

Differential thermal analysis (DTA) is technique for measuring the heat effects associated with physical or chemical change that takes place when a substance is heated at constant rate.

The basic principle of the differential thermal analysis is the measurement of the temperature difference between the sample and reference material as they are simultaneously heated at a uniform rate.

A micro DTA apparatus of ashimadzu DT-50 model was used for the measurement Differential thermal analysis. The studied samples consisted of 10 mg in a powder form.

X-ray diffraction can be used to identify a material and give information about the phase, lattice stress, and grain size [4,5].

4.4Sample preparation:

Different samples were prepared from Manganese Sulfide under different temperatures as below:

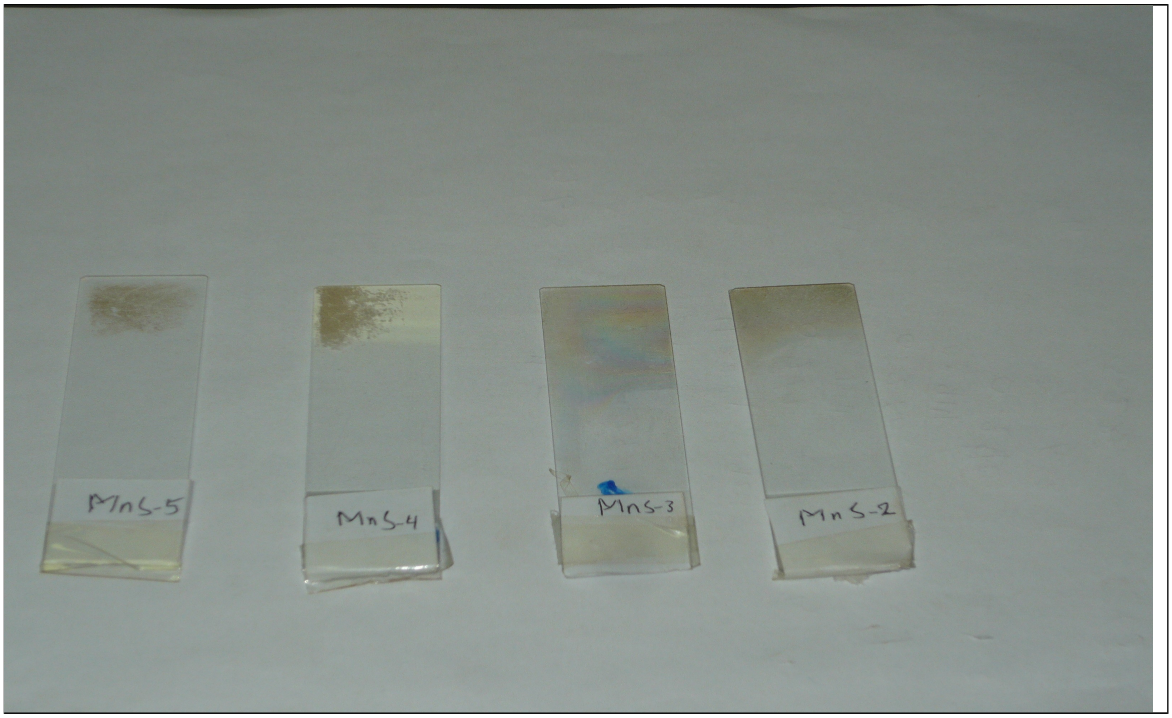
Tables 4.2.Conditions under which the Samples were prepared:

Sample No	Sample Name	Treatment (period (min	Pressure ((mbar	Treatment temperature ((C^o
1.	MnS-1	30	2×10^{-7}	50,100,150,200
2.	MnS-2	30	2×10^{-7}	50,100,150,200
3.	MnS-3	30	2×10^{-7}	50,100,150,200
4.	MnS-4	45	2×10^{-7}	50,100,150,200
5.	MnS-5	45	2×10^{-7}	50,100,150,200

4.5 The methods of MnS thin films deposition:

Manganese sulfide was chosen to produce thin film. MnS was put in boat see figure 4.2, these boat was connected to holder which carried high current heater, the substrate which is made of glass was adjusted perfectly directly up to source material, after this the chamber closed then the steps of pumping was began after (2) hours was arrived to pressure 2×10^{-7}torr, then began to increased upon this process the compound was transform solid face to gaseous, then the film be formed in the substrate.

For heat treatment of samples electrical furnace was used, The processes of samples, MnS-1, MnS-2, MnS-3, MnS-4, MnS-5 at room temperature and 50C^0, 100C^0, 150C^0, 200C^0 respectively in variation times (30& 45 minute).



Figures 4.6 sample of (MnS) substrate on glass

4.6 Methods of thickness measurement:

The film thickness is a very important parameter affecting the optical properties of the films. Therefore, it may be measured during deposition or post deposition.

After the apparatus was arranged the light was focused on abeam splitter and it divided into two beams. One of them transmitted to the first mirror, on the other is reflected to the second one. The two beams are interfered as a result of the reflection of the light once again to consist of the interference patterns. The lens was placed in front of laser source and it moved until the clear fringes (Newton rings) was appearing. After that the substrate was placed on the holder. The light must be incident to the region between (MnS) layer and the etched one. Due to difference in the thickness of thin film layers the patterns of the interference were shifted (it defected from paths by (ΔD) [55,56and 57].

4.7Transmission and reflection measurement:

To measure transmission and reflection intensity alight beam is directed towards each sample. The transmitted intensity is measured directly by using UV Vis Spectrophotometer.

The transition and reflection can given by:

$$T = \frac{I_T}{I_O} \qquad (4.5.1)$$

$$R = \frac{I_R}{I_O} \qquad (4.5.2)$$