Taungoo University Research Journal 2014, Vol. 5,No.1

Some Nickel Sulphide Thin Films and Their Structural Analysis

Zaw Win

Abstract

Thin films of Nickel Sulphide (NiS and NiS_2) were grown on glass substrates at room temperature and 50 °C for NiS and 55 °C for NiS_2 using Chemical Bath Deposition (CBD) technique. In the first compound (NiS), the chemical bath contained nickel sulphate ($NiSO_4$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and triethanolamine ($C_6H_{15}NO_3$) solutions. The aim of the present study was to analyze the different experimental conditions to prepare NiS thin films using chemical bath deposition technique. The properties of the films varied with the variation in the deposition parameters. The films deposited at longer deposition time showed improved crystallinity and better adhesion to the substrate. In the second one (NiS_2), nickel chloride hexahydrate ($NiCl_2.6H_2O$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and ammonia (NH_3) solutions were mixed at 55 °C in the chemical bath. Four samples of the films were annealed at temperatures of 100 °C, 200 °C, 300 °C and 400 °C while one sample was un-annealed to serve as a reference. The structural properties of nickel sulphide thin films were observed by X-ray diffraction.

Introduction

There has been a growing interest in the binary compounds because of their electronic and optical applications. Nickel sulphide thin films (NiS) belong to VIII-VI compound semiconductor materials. They have a number of applications in various devices such as solar cells, sensors, photoconductors and infrared detectors. A variety of methods, including electrodeposition, SILAR, pulsed laser ablation, metal-organic chemical vapour deposition, thermal and photochemical chemical vapour deposition can be used for the preparation of nickel sulphide thin films. Chemical bath deposition method is an attractive choice due to its simplicity, low cost, low temperature and potential for large-scale production. Up-to-date, chemical bath deposition method has been successfully used to deposit many different semiconductors thin films including CdS, Sb_2S_3 and CdSe, Cu_4SnS_4 and $Zn_xCd_{1-x}S$. So far, there is no report on deposition of NiS thin films from aqueous solution using triethanolamine as complexion agent at room temperature and 50°C by chemical bath deposition method. The influences of deposition time and low temperature on the properties of thin films were studied. The results of the investigation on structural properties of thin films have been carried out by using X-ray diffraction.

Nickel sulphide (NiS_2) thin films also belong to group VIII- VI compound semiconductor materials and have diverse applications in the areas of optoelectronics and electro-optic devices. The deposition of chalcogenide thin films has been carried out by many researchers using CBD techniques, sol-gel method, vacuum evaporation, radio frequency sputtering, cathodic electron deposition, etc. The CBD technique, as used in this work, remains one of the simplest, efficient and cost effective methods that yield desirable results including deposition on different kinds of substrates, shapes and sizes. Following the successful deposition of the NiS_2 thin films, four samples were annealed at various temperatures and diverse effects of annealing on solid state properties of the thin films are reported in this work.

Lecturer, Department of Physics, Taungoo University

Experimental

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionized water. The nickel sulphide thin films (NiS) were prepared from aqueous solutions of nickel sulphate ($NiSO_4$) and sodium thiosulphate ($Na_2S_2O_3.5H_2O$) acted as a source of Ni^{2+} and S^{2-} ions, respectively. Triethanolamine (TEA) was used as complexing agent during deposition. The glass substrates were used as the substrates for the chemical bath deposition of nickel sulphide thin films. Before deposition, the glass substrates were degreased with acetic acid and soap, and rinsed with water. Then, they were cleaned with acetone. Finally, they were washed with distilled water and dried in oven for 10 min.

Deposition of thin films was carried out at room temperature and 50 °C in the following manner. 25 ml of $NiSO_4$ (1.0 M) was taken in a 100 ml beaker and 16.7 ml of concentrated TEA was mixed in it. Subsequently, 25 ml of $Na_2S_2O_3.5H_2O$ (1.0 M) and 10 ml of distilled water were added in it with constant stirring. The cleaned glass substrates were immersed vertically into beaker. The deposition was carried out at different deposition times (1, 2 and 3 hours) at room temperature and 50°C in order to determine the best conditions for the deposition of thin films. After the completion of deposition, the films were removed from the beaker and dried in air for 10 hours before analysis.

The Nickel Sulphide thin films (NiS_2) were prepared from aqueous solution of nickel chloride ($NiCl_2.6H_2O$) and sodium thiosulphate ($Na_2S_2O_3.5H_2O$) as sources of Ni^{2+} and S^{2-} ions respectively. Ammonia (NH_3) solution was used as a complexing agent during the deposition. Cleaning methods for glass substrates were the same as that in NiS compound. The cleaned glass substrates were then inserted vertically in the reaction bath.

The composition of the 100 ml bath consists of 5ml of $NiCl_2.6H_2O$ (1.0 M) solution, 15 ml of $Na_2S_2O_3.5H_2O$ (1.0 M), 10 ml of NH_3 and 30 ml of distilled water. The mixture was stirred thoroughly with magnetic stirrer (IKA® C-MAG HS 7) at each stage and made up to 90 ml with distilled water. For optimization of the thin films, four different mixtures using $NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml, (5:15:15) ml, (5:20:15) ml, (10:10:20) ml] were prepared in an oven at 55 °C and left undisturbed for six hours. The deposited thin film samples were then annealed in an oven heating at temperatures of 100 °C, 200 °C, 300 °C and 400 °C leaving one un-annealed sample. All the samples were further washed in distilled water and air-dried for analysis.

Results and Discussion

The structure of the films were observed by X-ray diffraction (XRD) with a Rigaku (MultiFlex) X-ray diffractometer equipped with CuK_α (λ= 1.5418 Å) radiation source. Data were collected by step scanning from 10° to 70° with a step size of 0.02°/ 0.06 (sec). The setting parameters were 40 kV and 40 mA.

Fig 1, Fig 2 and Fig 3 show XRD patterns of nickel sulphide thin films (NiS) grown at room temperature for 1, 2 and 3 hours respectively. The comparison of the observed diffractions peaks with the standard (JCPDS reference code: 75-0612, 89-1957) confirmed that the material exhibits the hexagonal structure of nickel sulphide. Comparison between the films deposited at different time reveals that the intensities of the peaks increased, indicating better crystalline phase in the films prepared at longer deposition time. This could be seen in the peak attributable to (1 0 1) plane, which is more intense. On the other hand, some peaks are belong to $Ni(OH)_2$ (JCPDS reference code: 73-1520). These peaks come from the reaction of Ni^{2+} ions and OH^- ions from the solution. Fig 4, Fig 5 and Fig 6 also describe the same phenomena of NiS at 50°C for 1, 2 and 3 hours respectively. The intensities of the peaks at 50°C were slightly more intense than that at room temperature. Therefore, longer deposition time and low temperature effects show better crystalline phase for optimization of the thin films.

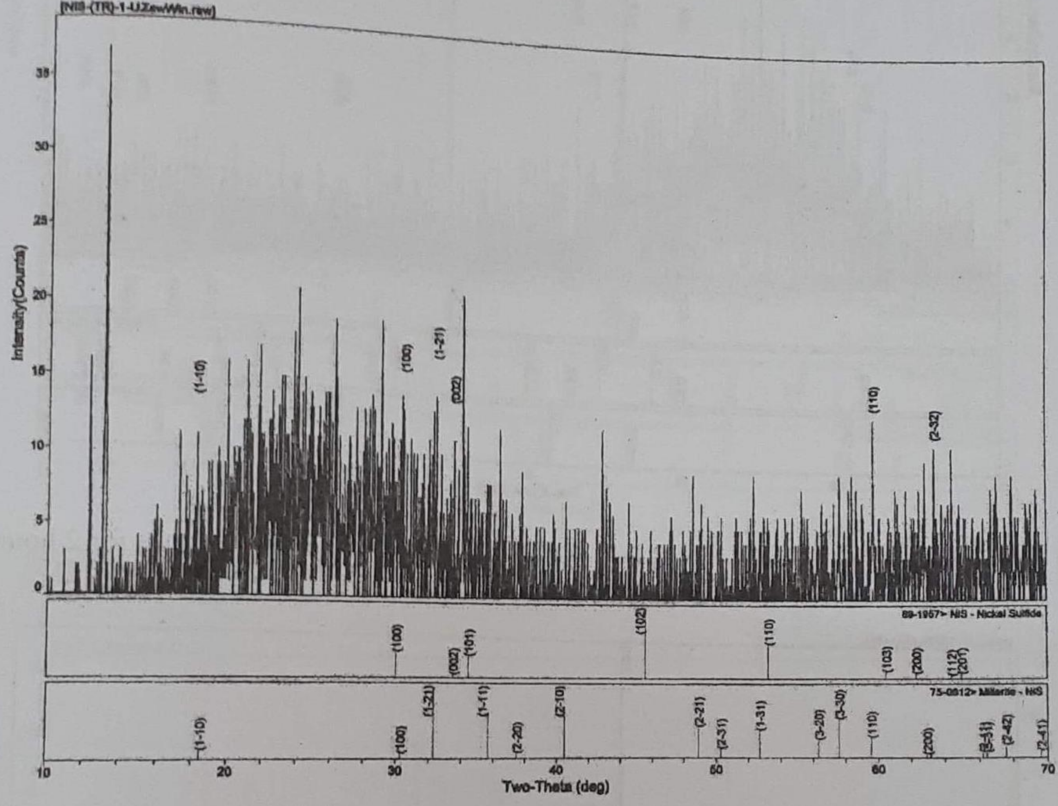

Fig 1 X-ray diffraction pattern of NiS thin film deposited at room temperature for 1 hour

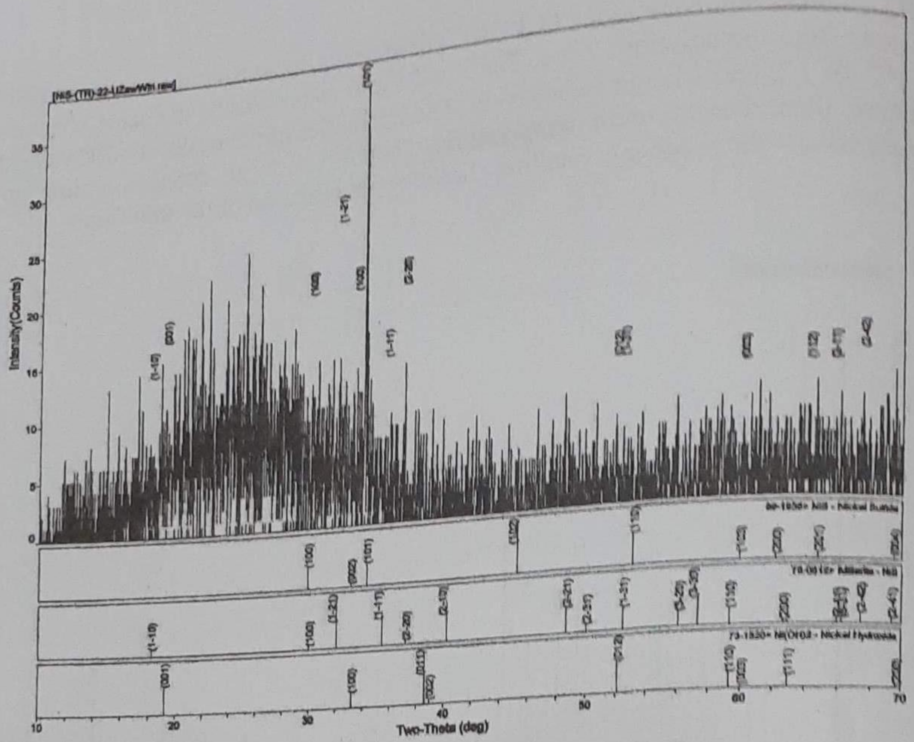

Fig 2 X-ray diffraction pattern of NiS thin film deposited at room temperature for 2 hours

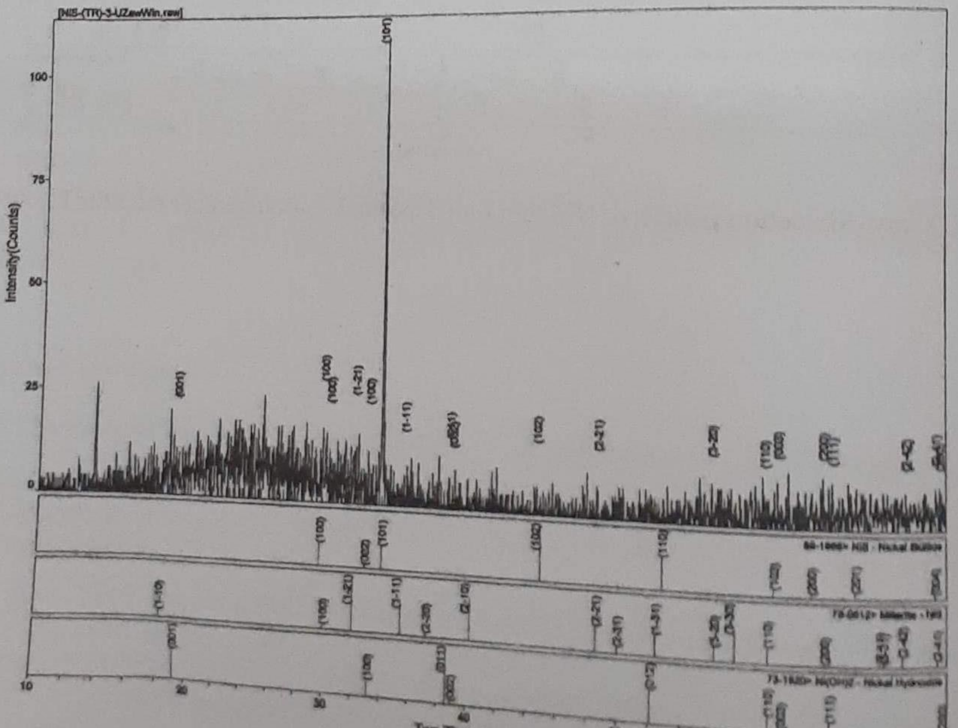

Fig 3 X-ray diffraction pattern of NiS thin film deposited at room temperature for 3 hours

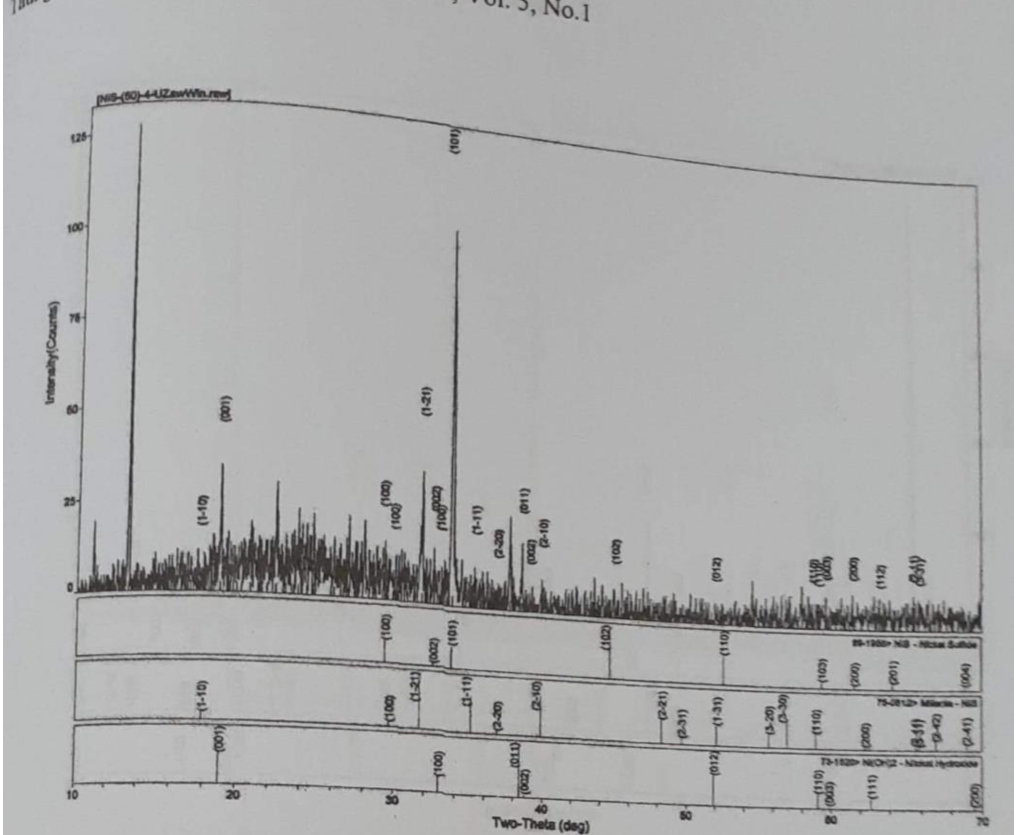

Fig 4 X-ray diffraction pattern of NiS thin film deposited at 50°C for 1 hour

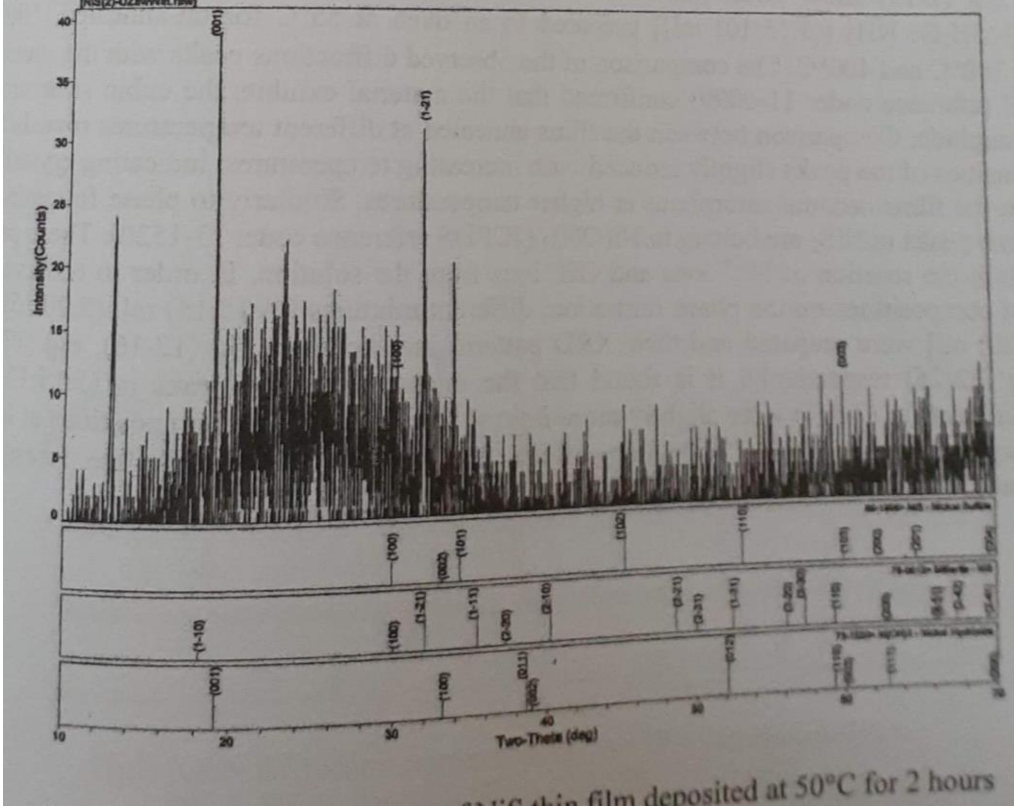

Fig 5 X-ray diffraction pattern of NiS thin film deposited at 50°C for 2 hours

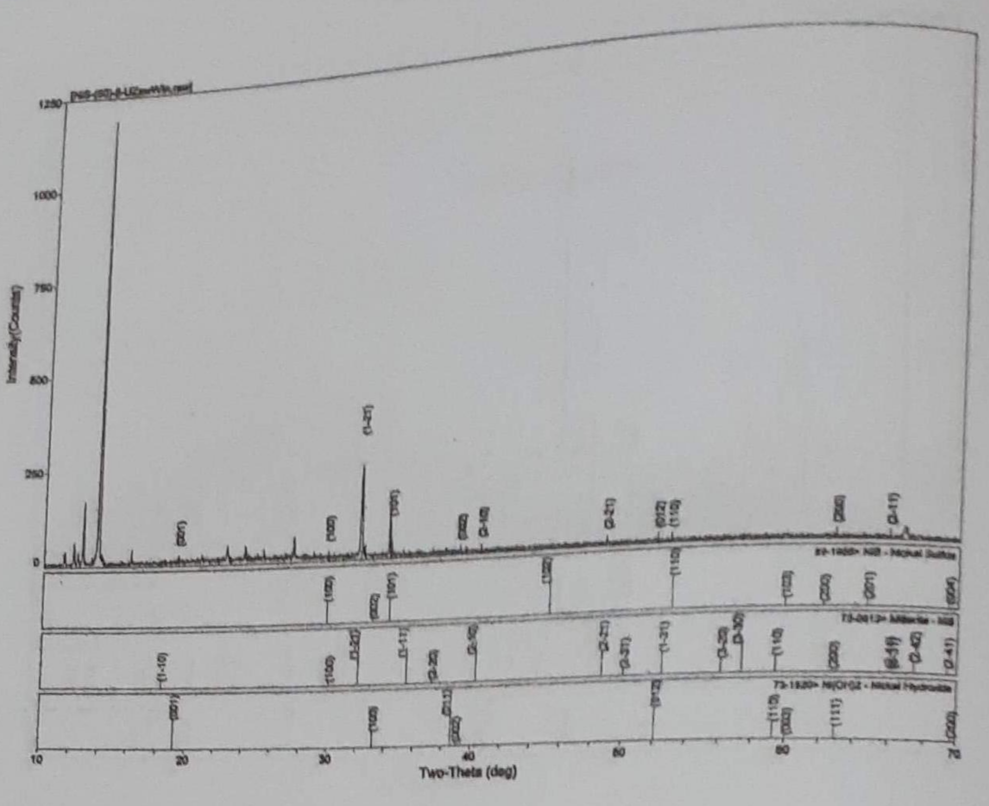

Fig 6 X-ray diffraction pattern of NiS thin film deposited at 50°C for 3 hours

Fig (7-11) show XRD patterns of nickel sulphide thin films (NiS_2) [$NiCl_2.6H_20$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]] prepared in an oven at 55°C for un-annealed, 100°C, 200°C, 300°C and 400°C. The comparison of the observed diffractions peaks with the standard (JCPDS reference code: 11-0099) confirmed that the material exhibits the cubic structure of nickel sulphide. Comparison between the films annealed at different temperatures reveals that the intensities of the peaks slightly reduced with increasing temperatures, indicating crystalline phase in the films become amorphous at higher temperatures. Similarly to phase formation in NiS, some peaks in NiS_2 are belong to $Ni(OH)_2$ (JCPDS reference code: 73-1520). These peaks come from the reaction of Ni^{2+} ions and OH^- ions from the solution. In order to observe the effect of compositions on the phase formation, different mixtures [(5:15:15) ml, (5:20:15) ml, (10:10:20) ml] were prepared and their XRD patterns are shown in Fig (12-16), Fig (17-21) and Fig (22-26) respectively. It is found that the intensities of the peaks in (5:15:10) ml compositions (Fig (7-11)) were slightly more intense than that of other compositions at lower annealing temperatures. So, annealing effects also show better crystalline phase for optimization of the thin films.

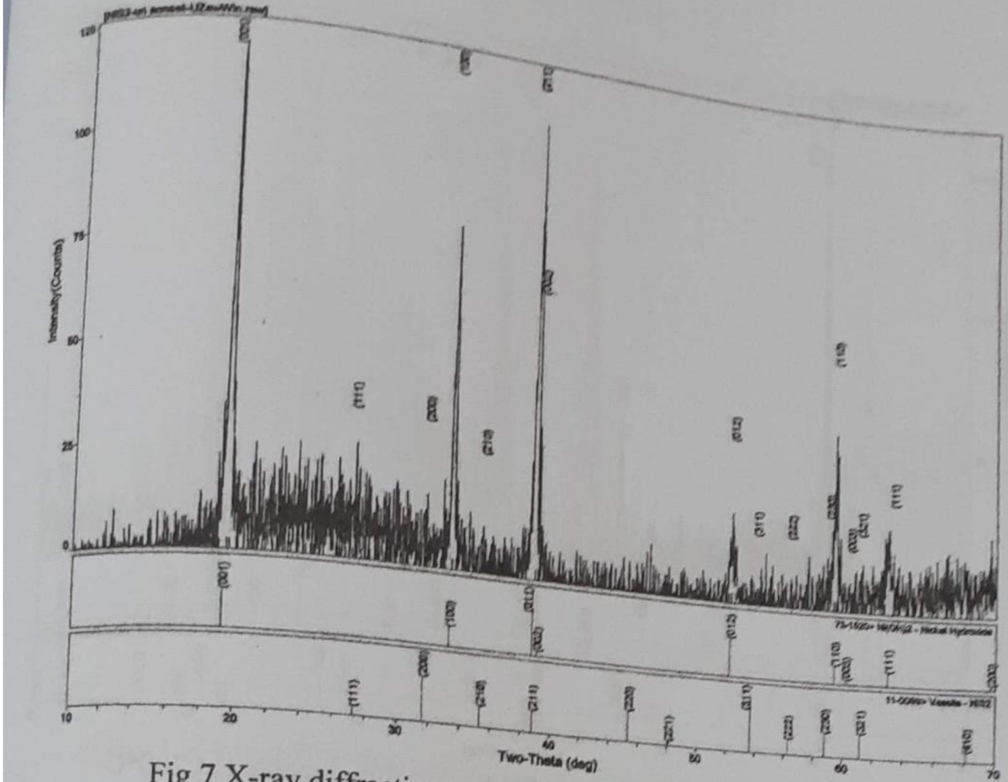

Fig 7 X-ray diffraction pattern of NiS_2 thin film un-annealed [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]]

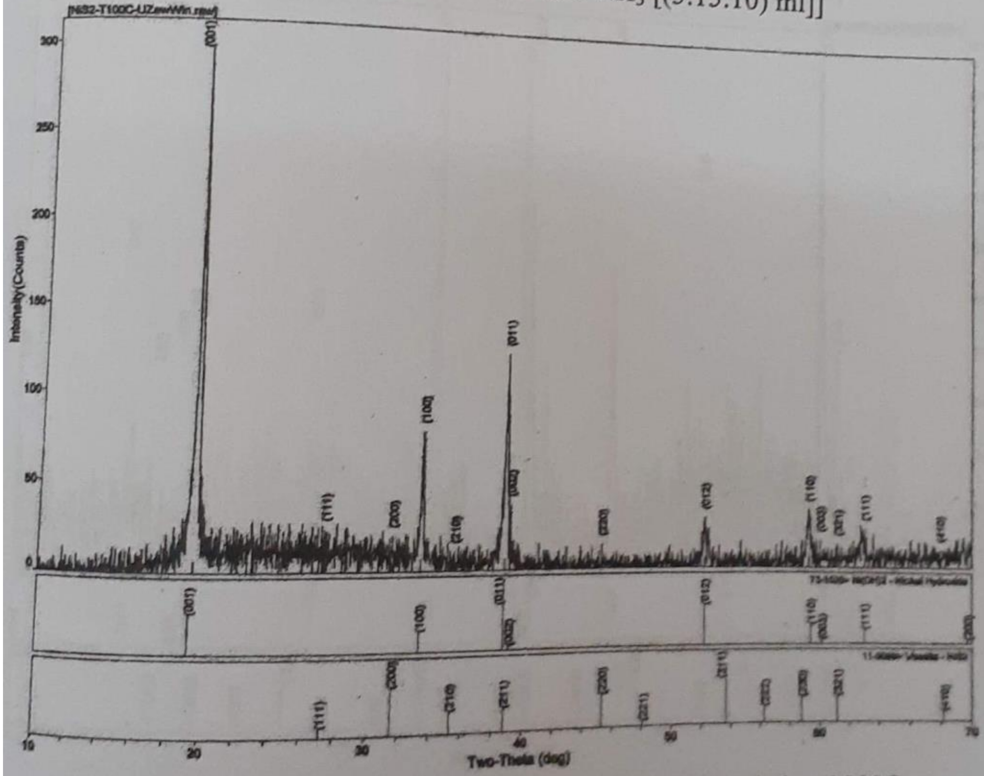

Fig 8 X-ray diffraction pattern of NiS_2 thin film annealed at 100°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]]

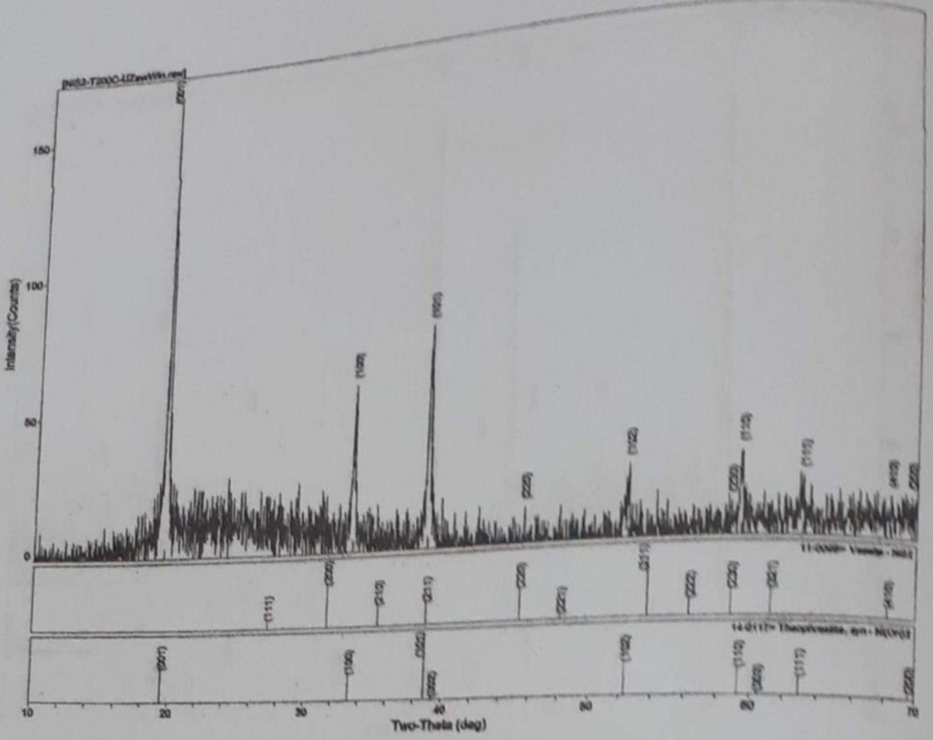

Fig 9 X-ray diffraction pattern of NiS_2 thin film annealed at 200°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]]

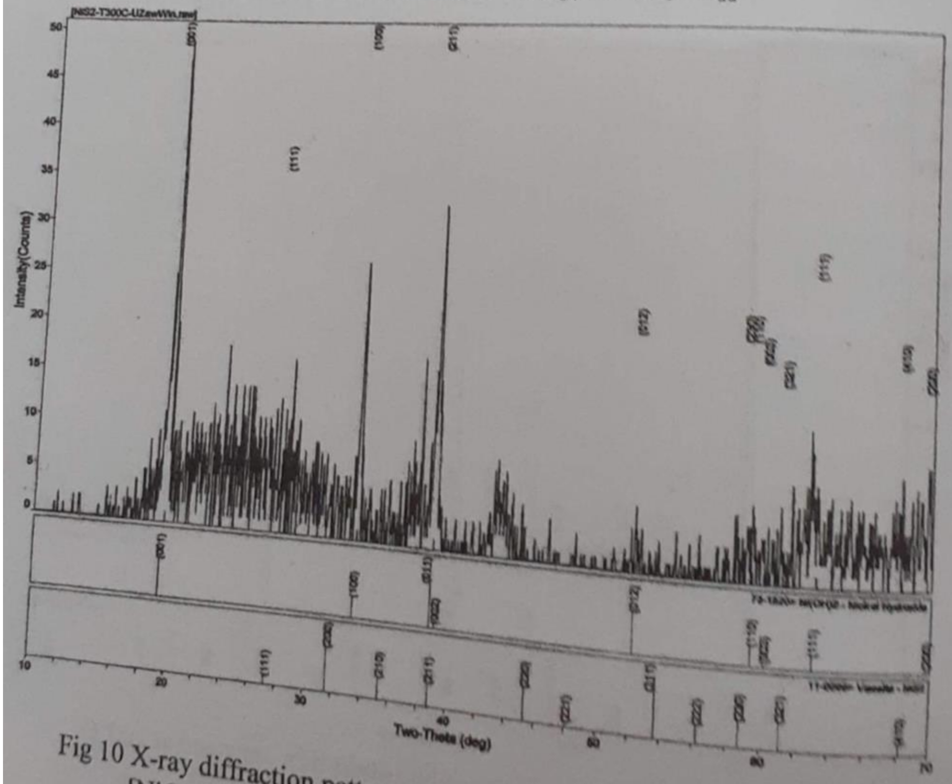

Fig 10 X-ray diffraction pattern of NiS_2 thin film annealed at 300°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]]

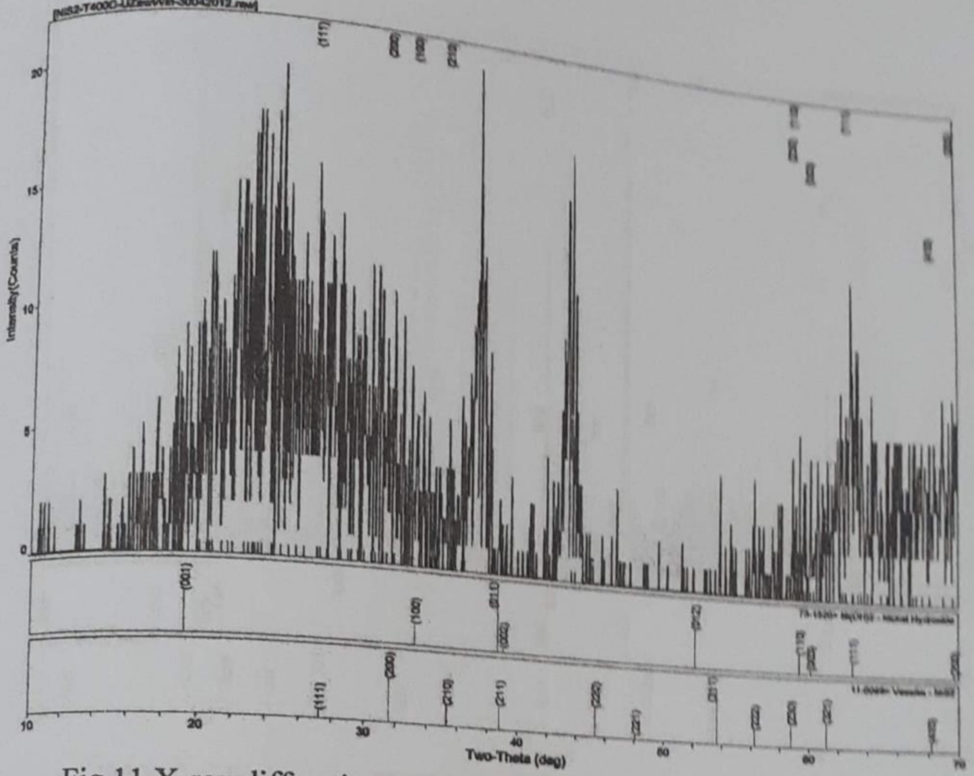

Fig 11 X-ray diffraction pattern of NiS_2 thin film annealed at 400°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:10) ml]]

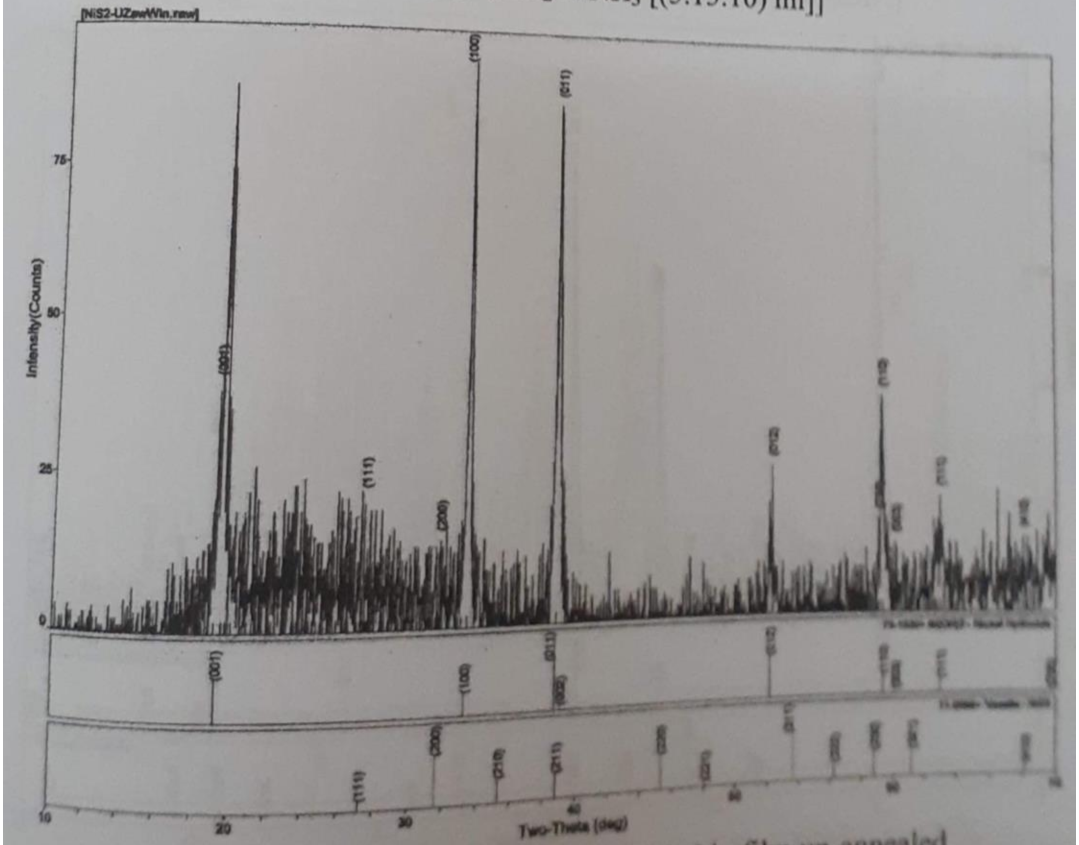

Fig 12 X-ray diffraction pattern of NiS_2 thin film un-annealed [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:15) ml]]

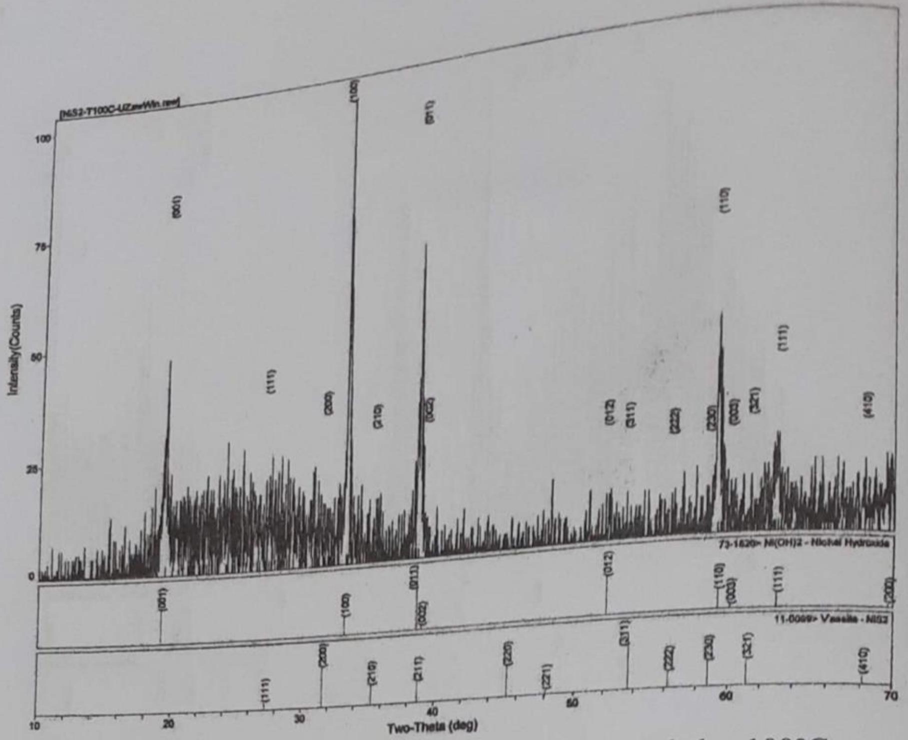

Fig 13 X-ray diffraction pattern of NiS_2 thin film annealed at 100°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:15) ml]]

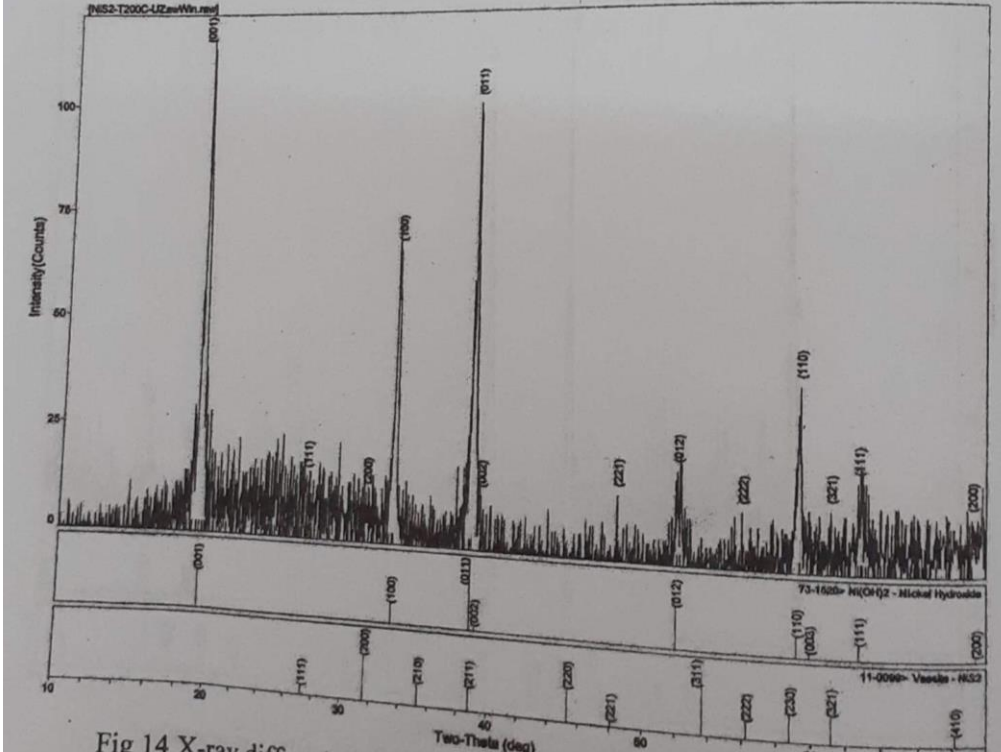

Fig 14 X-ray diffraction pattern of NiS_2 thin film annealed at 200°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:15) ml]]

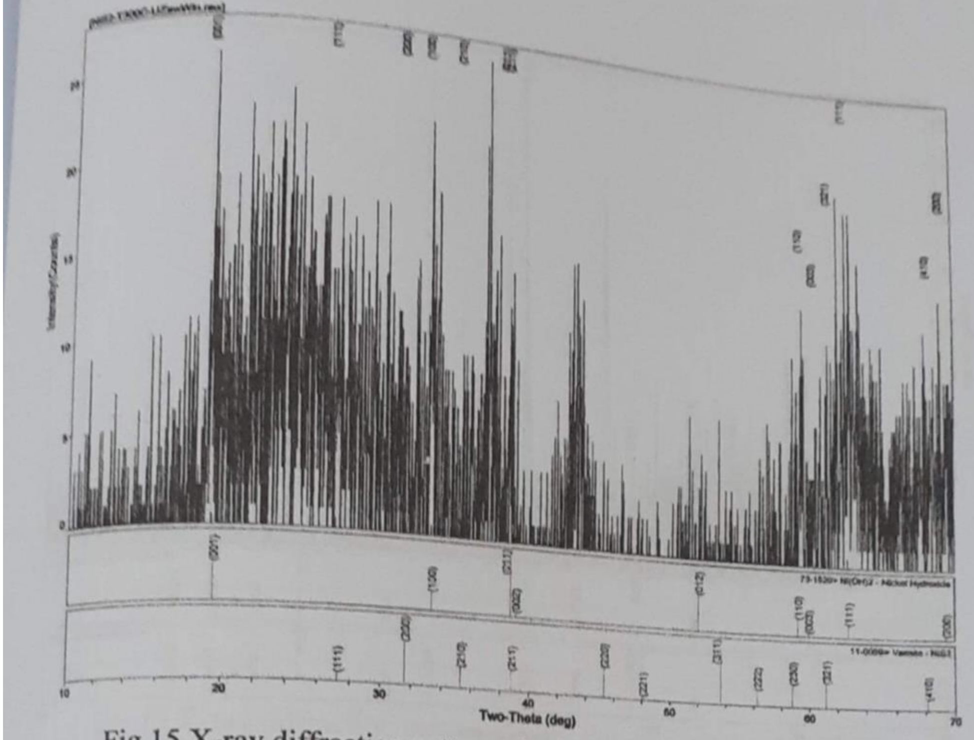

Fig 15 X-ray diffraction pattern of NiS_2 thin film annealed at 300°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:15) ml]]

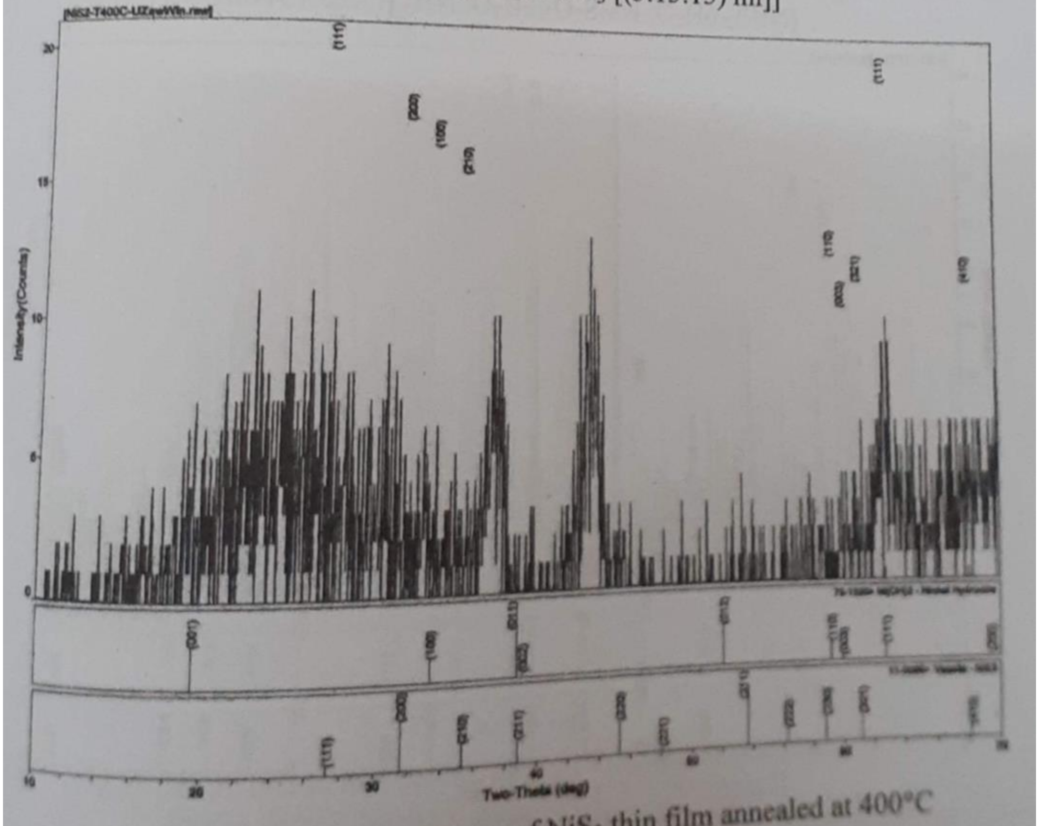

Fig 16 X-ray diffraction pattern of NiS_2 thin film annealed at 400°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:15:15) ml]]

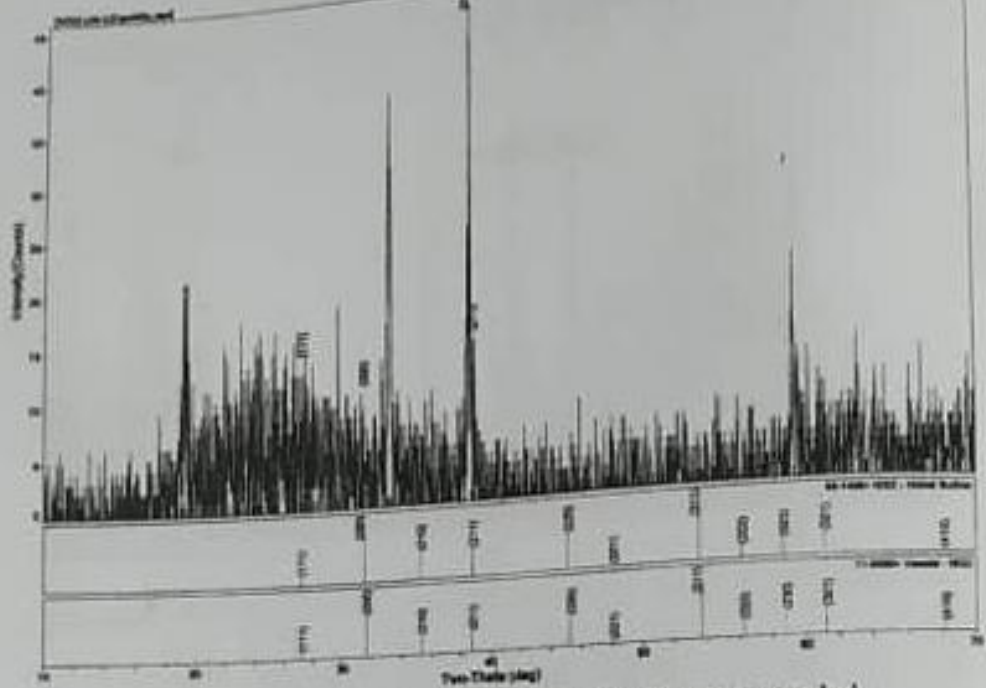

Fig 17 X-ray diffraction pattern of NiS_2 thin film un-annealed
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:20:15) ml]

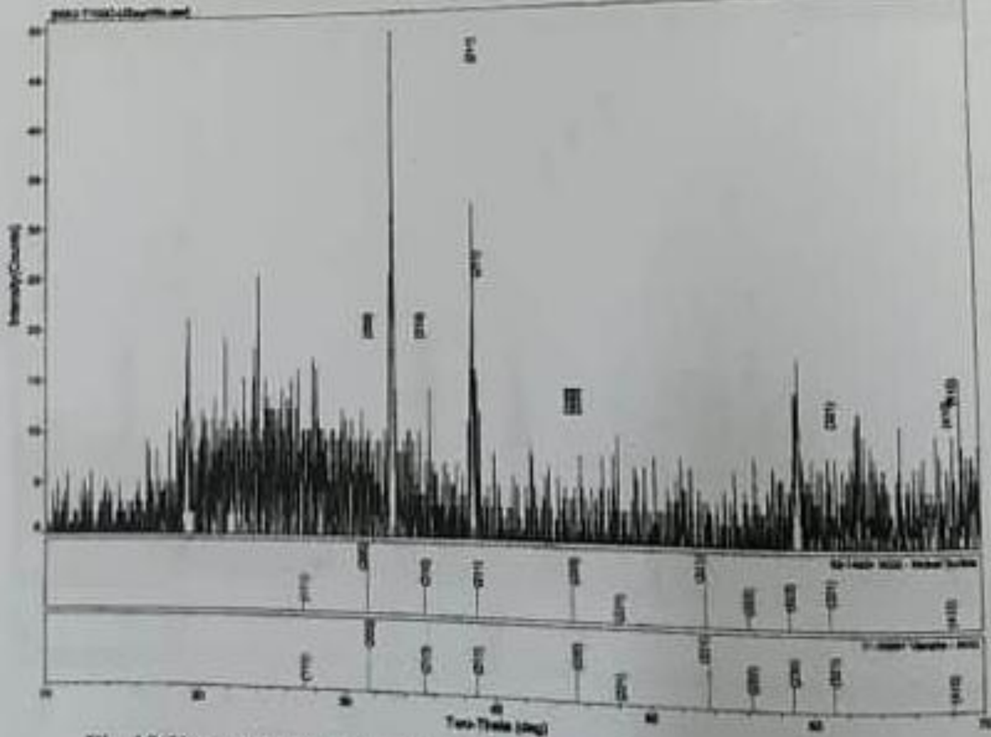

Fig 18 X-ray diffraction pattern of NiS_2 thin film annealed at 100°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:20:15) ml]

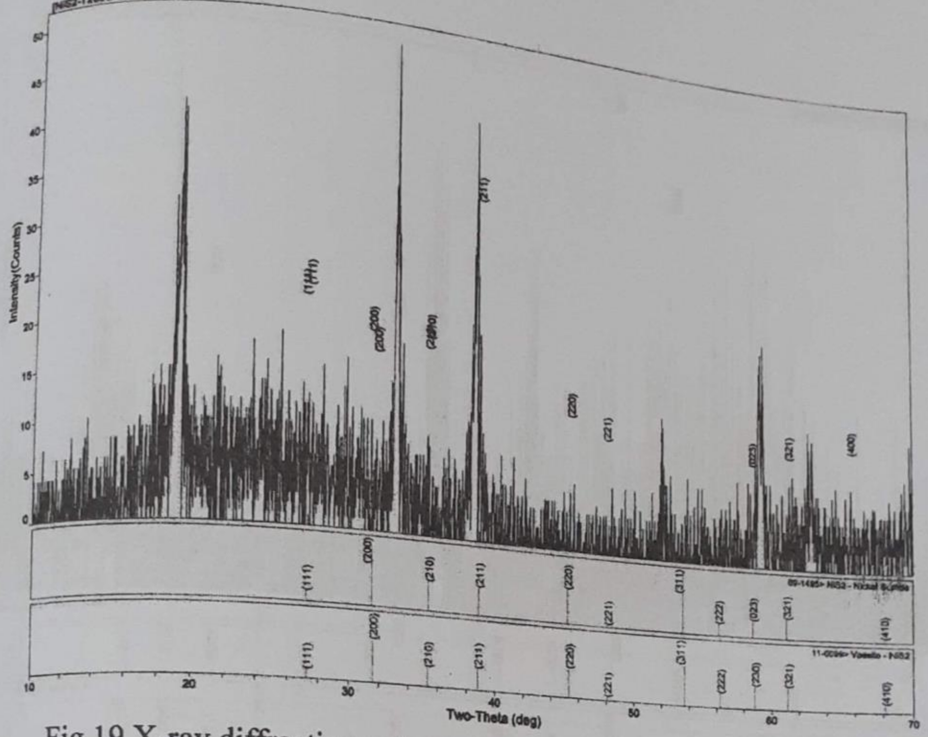

Fig 19 X-ray diffraction pattern of NiS_2 thin film annealed at 200°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:20:15) ml]

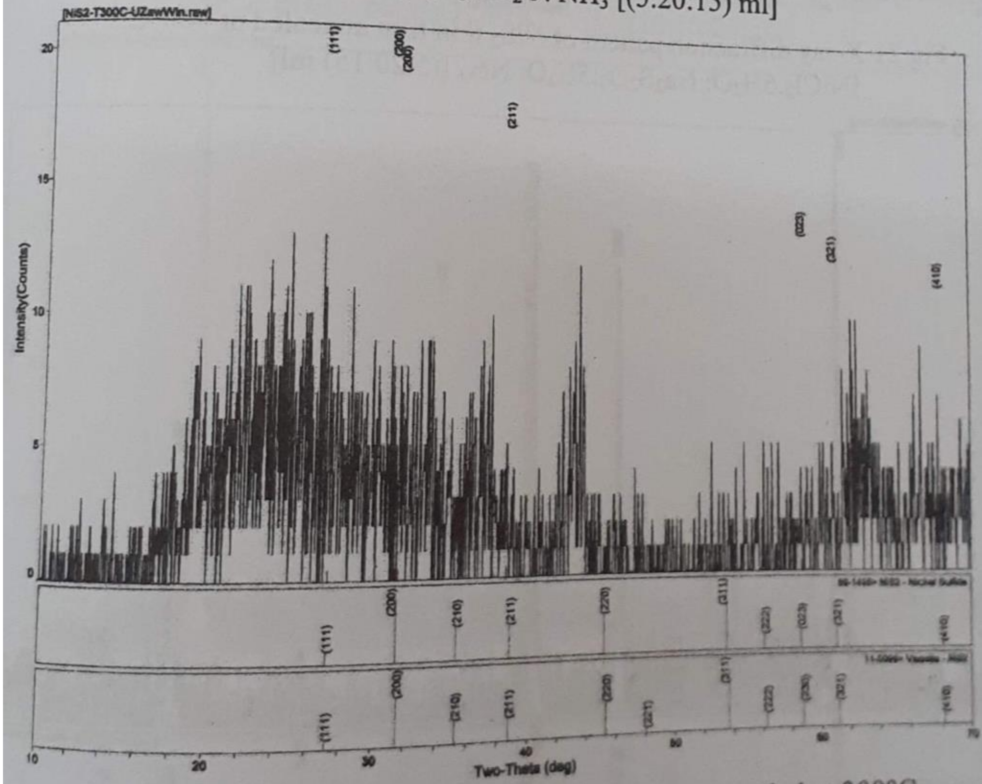

Fig 20 X-ray diffraction pattern of NiS_2 thin film annealed at 300°C [$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:20:15) ml]

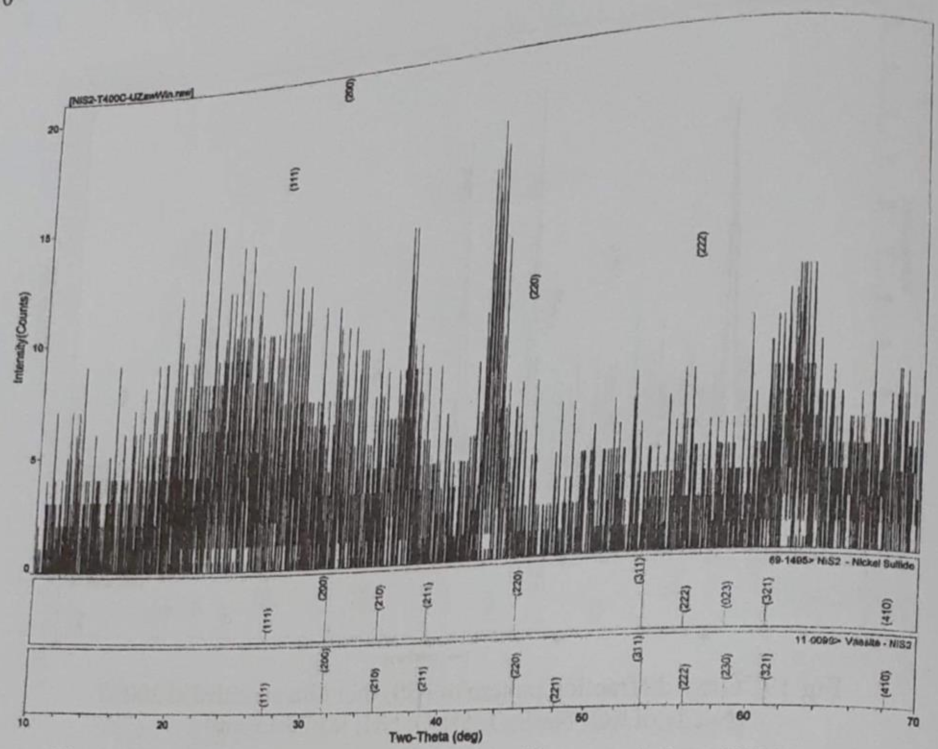

Fig 21 X-ray diffraction pattern of NiS_2 thin film annealed at 400°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(5:20:15) ml]

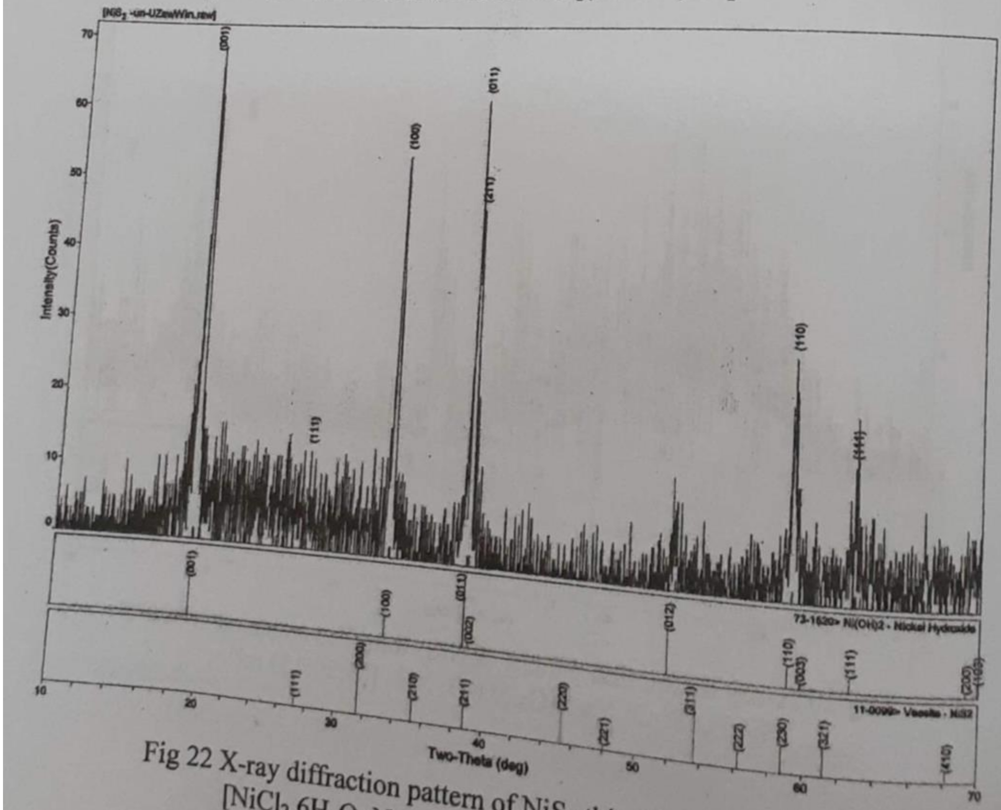

Fig 22 X-ray diffraction pattern of NiS_2 thin film un-annealed
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(10:10:20) ml]

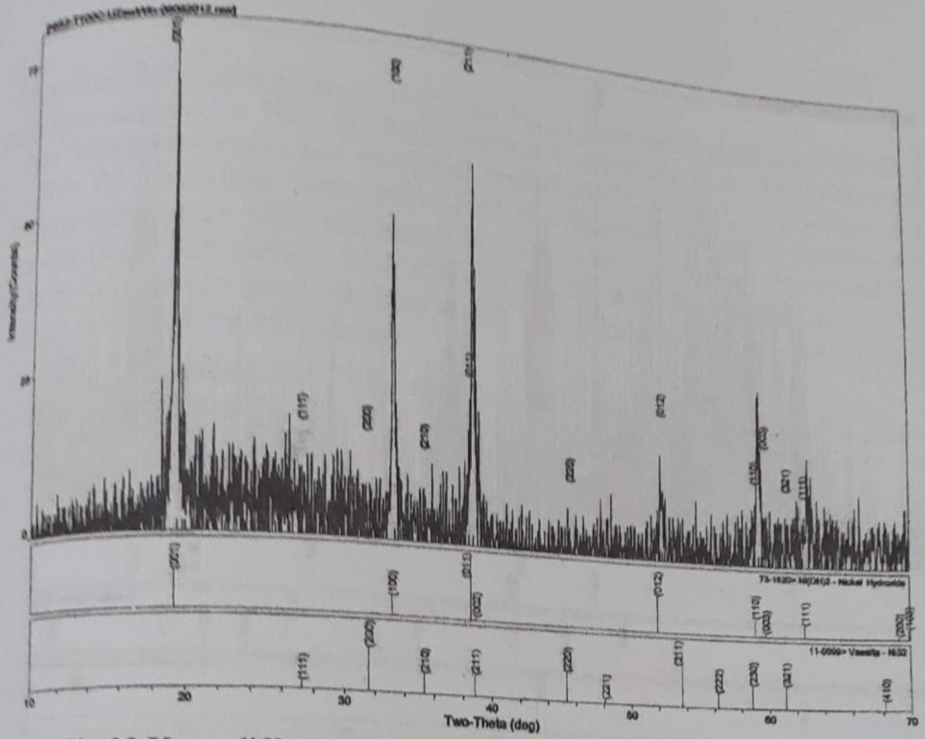

Fig 23 X-ray diffraction pattern of NiS_2 thin film annealed at 100°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(10:10:20) ml]

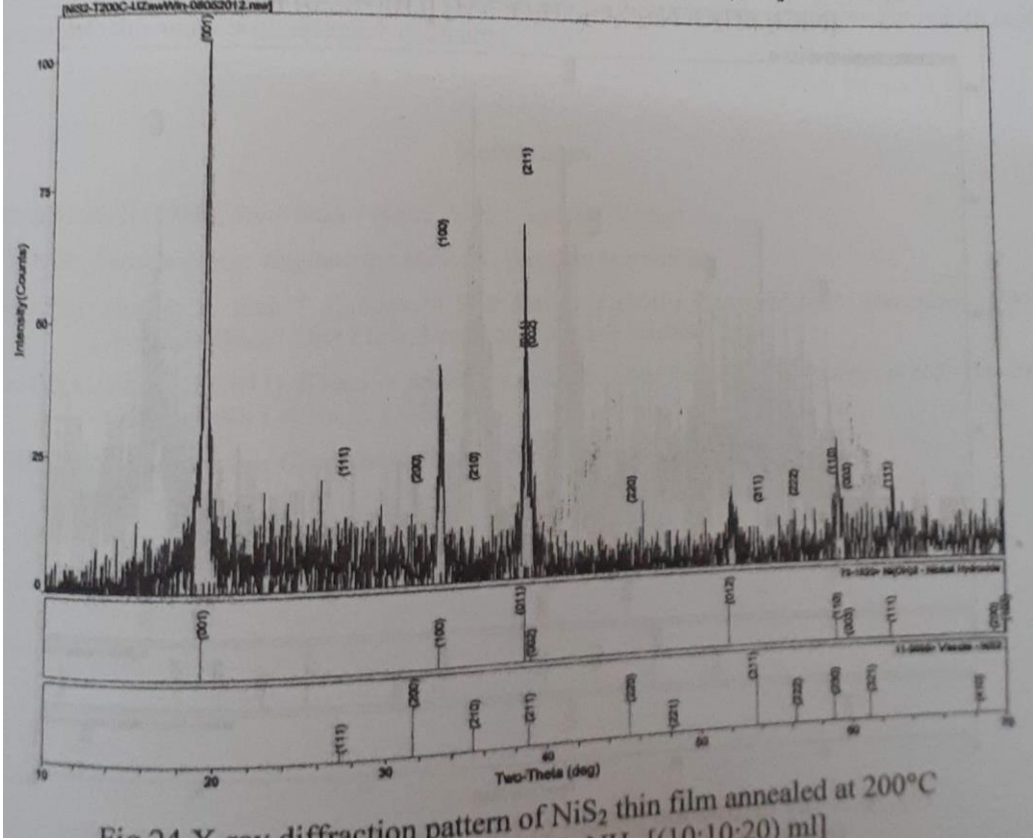

Fig 24 X-ray diffraction pattern of NiS_2 thin film annealed at 200°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(10:10:20) ml]

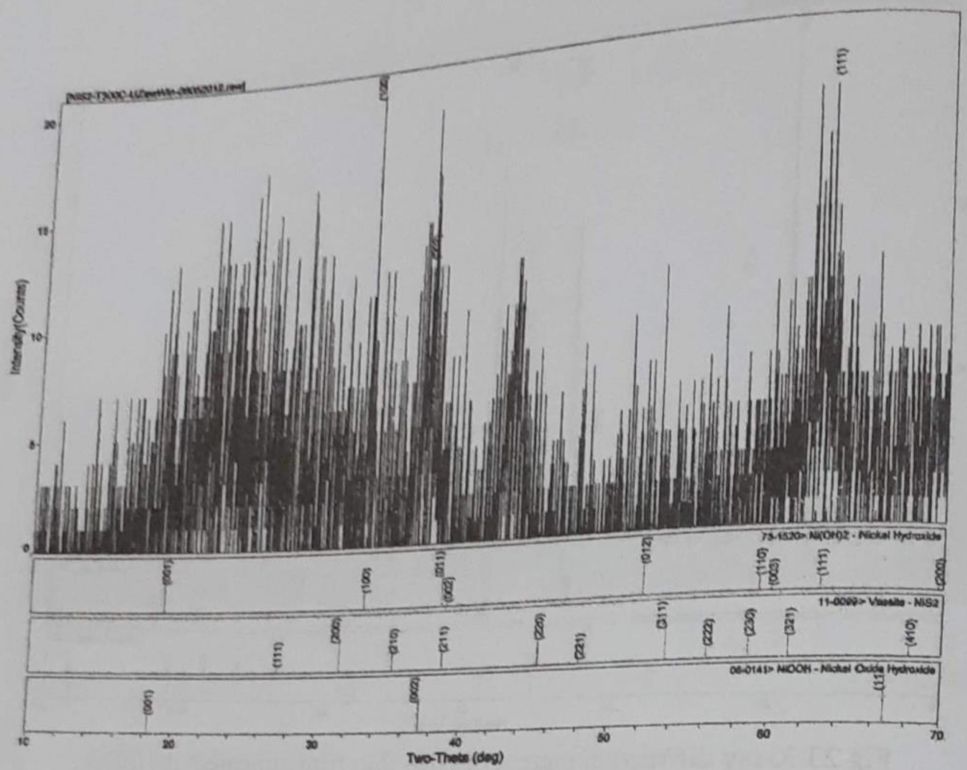

Fig 25 X-ray diffraction pattern of NiS_2 thin film annealed at 300°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(10:10:20) ml]

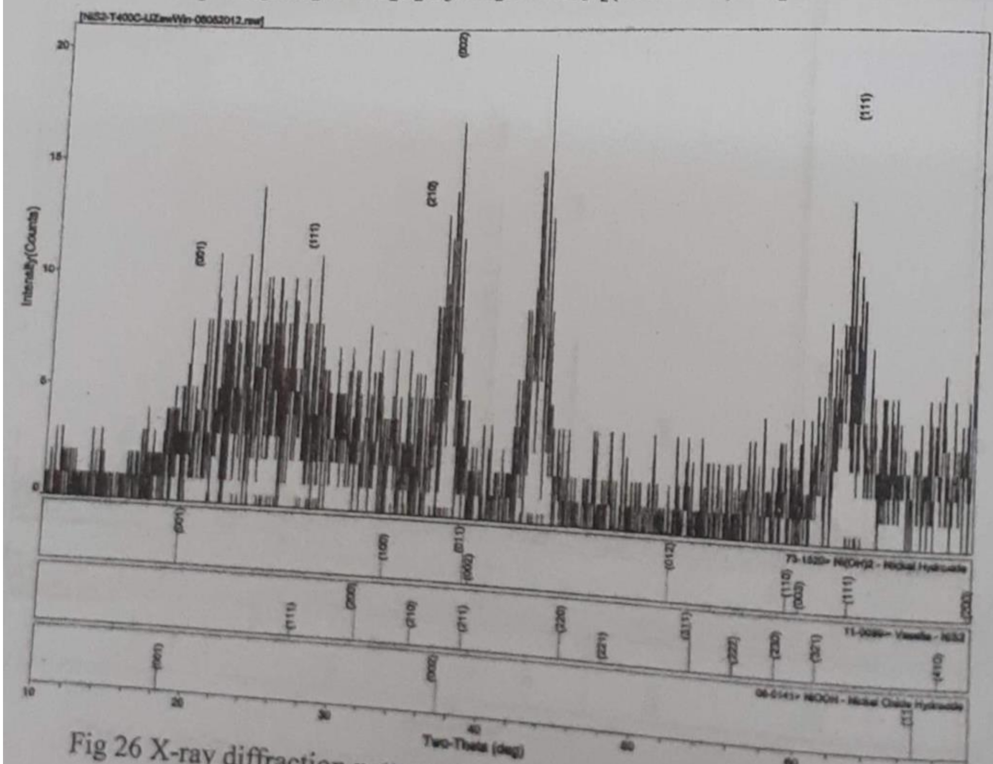

Fig 26 X-ray diffraction pattern of NiS_2 thin film annealed at 400°C
[$NiCl_2.6H_2O$: $Na_2S_2O_3.5H_2O$: NH_3 [(10:10:20) ml]

Conclusion

Thin films of nickel sulphide (NiS and NiS_2) have been synthesized using chemical bath deposition method. In NiS, the XRD patterns showed the films were polycrystalline in nature with hexagonal phase and exhibited preferentially along (1 0 1) direction. It was observed that the deposition parameters could significantly change the crystallinity of the films. At low temperature 50°C and longer deposition time (3 hours), the crystallinity of the films was improved. According to XRD results, it is concluded that the best quality of NiS thin films have been grown on glass substrate at 50°C and deposition time (3 hours) using 1 M of nickel sulphate and sodium thiosulphate.

For NiS_2 as grown and NiS_2 annealed at low temperature samples exhibit better crystallinity and those annealed at high temperature samples become amorphous. Therefore, annealing at low temperature provides better crystalline phase for optimization of the thin films.

Acknowledgements

I would like to express my thanks to Rector, Pro-rector, Taungoo University, for their kind permission to carry out this work.

I am greatly indebted to Associate Professors, Department of Physics, Taungoo University, for their valuable guidance.

Finally, I also owe a great deal to my colleagues for their support encouragement, which enable me to complete this work without much difficulty.

References

Ibach H and Luth H (1990), *Solid State Physics* (Berlin: Springer-Verlag)

John V (1992), *Introduction to Engineering Materials* (London: Macmillan)

Kassim A, Nagalingam S, Wee T T, Soon M H & Darren T (2010), *Chemical Bath Deposition of Nickel Sulphide (Ni_4S_3) Thin Films*, Leonardo Journal of Sciences, 16, 1

Osuwa J C & Uwaezi P U (2011), *Effects of Annealing on Optical and Solid State Properties of NiS_2 Thin Films*, Chalcogenide Letters, 8, 9, 587

Sandra E D (2000), *Reaction and Characterization of Solids* (Bristol: Polestar Wheatons)