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STUDY OF STRUCTURAL PROPERTIES OF MULTILAYER ZNS THIN FILMS

Jitendra singh[1],Pushpendra Singh[2],Kapil Sirohi[3],Shekher Singh[4]

[1]Dept.of Physics,K.G.K.(P.G.)College,Moradabad,(U.P.)India

[2]Dept.of Applied Science,TMU, Moradabad,(U.P.)India

[3]Dept.of Basic Education, Moradabad,(U.P.)India

[4]Dept.of Chemistry,Devta College,Morna,Bijnor(U.P.)India

ABSTRACT

In the present investigation, the films of Zinc Sulphide and Polyaniline have been prepared by vacuum Evaporation Technique. The growth and characterization of single layer and multilayer films have been done. In this paper, the study of X-Ray diffraction and SEM of multilayer ZnS/Polyaniline thin films has been done.

Keywords: - Polyaniline, Zinc sulphide, X-ray diffraction,SEM

1. Introduction

Conducting polymers have emerged as a very important class of materials because of their unique electrical, optical and chemical properties leading to the wide range of technological applications [1]. This class of materials provides tremendous scope for tuning of their electrical conductivity from semiconducting to metallic regime by way of doping (MacDiarmid and Epstein 1994; Wessling 1999) [2,3]. The unique properties of conducting polymers not only provide great scope for their applications but also have led to the development of new models to explain their observed properties, particularly various mechanisms of charge transport (Kaiser *et al* 1995, 1997)[4,5]. Among different conducting polymers, conducting polyaniline is the most extensively studied material due to the ease of synthesis, better environmental and thermal stabilities and greater scope of playing with chemistry to tailor their properties (Kumar *et al* 1996) [6]. However, when they are taken in the composite form their electrical as well as dielectric properties are altered from those of basic materials. A number of groups have reported studies on the electrical conductivity and dielectric properties of composites of a variety of conducting polymers (Yoon *et al* 1995; Yang *et al* 1996; Gangopadhyay *et al* 2001; Murugesan and Subramanian 2003) [11]. It has been shown that the conductivity of these heterogeneous systems depends on a number of factors such as the concentration of conducting fillers, their shape, size, orientation and interfacial interaction between filler molecules and host matrix (Kryszewaski 1991; Brosseau *et al* 2001)[12]. The geometrical shape of the dispersant governs the ability of conductive network formation which results in large increase in the conductivity (Troung *et al* 1994) [104]. Also, dispersant/matrix interactions and physical properties of the matrix influence the agglomeration of the dispersant phase which, in turn, affects the dielectric properties of the composites. In case of conducting polymers as fillers, the degree of cross-linking between the polymeric chains also affects the electrical properties in these composites (MacDiarmid and Epstein 1995). Although the percolation theory has been generally used to explain the behaviour of electrical conductivity and dielectric properties of conducting polymer composites (Tuncer *et al* 2002), [14] but it could not explain very low values of percolation threshold observed in many of the composite systems of conducting polymers. Wessling (1998) proposed a non-equilibrium theory for the composites of conducting polymers. This theory while accounting for the interfacial interactions between conducting polymers and host matrix could explain the observations of low percolation threshold.

ZnS is the II–VI family semiconductor, has wide band gap (3.65 eV) at room temperature and large excitation binding energy 60 meV, ZnS is an attractive semiconductor material especially in electronic and optoelectronic application.The dielectric constant of ZnS (wurtzite structure) is 8.75 at lower frequencies and 3.8 at higher frequencies. The molecular mass is 81.389 and the melting temperature is 1450 K [].

ZnS was used by Ernest Rutherford and others in the early years of nuclear physics as a scintillation detector, because it emits light on excitation by x-rays or electron beam, making it useful for x-ray screens and cathode ray tubes.It also exhibits phosphorescence due to impurities on illumination with blue or ultraviolet light.

Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through x-ray screens to glow in the dark products.When silver is used as activator, the resulting color is bright blue, with maximum at 450 nm. Manganese yields an orange-red color at around 590 nm. Copper provides long glow time and the familiar glow-in-the-dark greenish color. Copper doped zinc sulfide (ZnS+Cu) is also used in electroluminescent panels .

Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to over 12 micrometres. It can be used planar as an optical window or shaped into a lens. It is made as microcrystalline sheets by the synthesis from H2S gas and zinc vapor and sold as FLIR (Forward Looking IR) grade ZnS in a pale milky yellow visibly opaque form.This material when hot isostatically pressed (HIPed) can be converted to a water-clear form known as Cleartran (trademark). Early commercial forms were marketed as Irtran-2 but this designation is now obsolete. In this paper we have reported XRD, SEM, of the PANI on glass substrate and PANI on the ZnS thin film.

2. Sample Preparation of ZnS:- Thin films of ZnS have been prepared by vacuum deposition technique. For sample preparation Zinc Sulphide powder of 99.99%. purity was evaporated at about 115°C from a deep narrow mouthed molybdenum boat. Deposition was made on to highly cleaned glass substrate held at 200°C in a vacuum of 10^{-5} torr. The substrate was cleaned in aquaregia washed in distilled water and isopropyl alcohol (IPA). We have used glass substrate for the preparation of Zinc Sulphide.

3. Sample Preparation of Poly aniline:-Thin film of polyaniline have been prepared by vacuum evaporation technique, polyaniline is usually prepared by redox polymerization of aniline using ammonium perdisulphate, $(NH4)_2\ S_2O_2$ as on oxidant. Distilled aniline (0.02 M) is dissolved in 300 ml of pre-cooled HC1 (l.0M) solution, maintained at 0-50°C. A calculated amount of ammonium perdisulphate, (0.05M) dissolved in 200 ml of HCl (1M), pre-coated to 0-50° C, is added to the above solution. The dark green precipitate (ppt) resulting from this reaction is washed with HC1 (l.OM) uptil the green colour disappears. This ppt is further extracted with terta-hydofuran and NMP (N-Methyl Pyrolidinone) solution by soxhelf extraction and dried to yield the emeraldine salt. Emeraldine base can be obtained by heating the emeraldine salt with ammonia solution. Simultaneously, separate salt solution is prepared by dissolving the MX (M=Metal and X=Halide) in distilled water. The solution is then slowly added to the precooled polymer solution with constant stirring. The composite is then dried in an oven, at high temperature, to get the conducting polymer in the powder form. This powder is vacuum evaporated on to highly cleaned glass substrate as well as metallic substrate.

4. Characterization of PANI and PANI on ZnS Film:-

(i) X-Ray Diffraction.

X-ray diffraction is a very good non destructive technique to confirm and find the structure of a crystal. In figure 1, 2 and 3 the XRD pattern of pure polyaniline, XRD pattern of ZnS and XRD pattern of PANI on ZnS respectively, has been reported. The XRD pattern of pure Polyaniline in figure 4.1 shows its amorphous structure because no strong peak has been appeared in XRD pattern. In the XRD pattern of ZnS [fig 2], strong peaks appear at 2θ=31.5°, 34.3°, 36.1°, 47.4°, 56.4°and 62.9° which corresponds to (100), (002), (101), (102), (110), (103) planes, that confirms the hexagonal structure of ZnS. The peaks in the XRD patterns show that ZnS film has a poly crystalline hexagonal wurtzite Crystal structure. The XRD patterns of ZnS in fig. 2 shows that the highly intense (101) peak shows the most preferred orientation. Other peaks with less intensity shows less preferred orientations. In case of PANI on ZnS same preferred orientation is observed with modified intensity [fig.3]. In addition there is no second phase peak in XRD patterns for ZnS-composites.

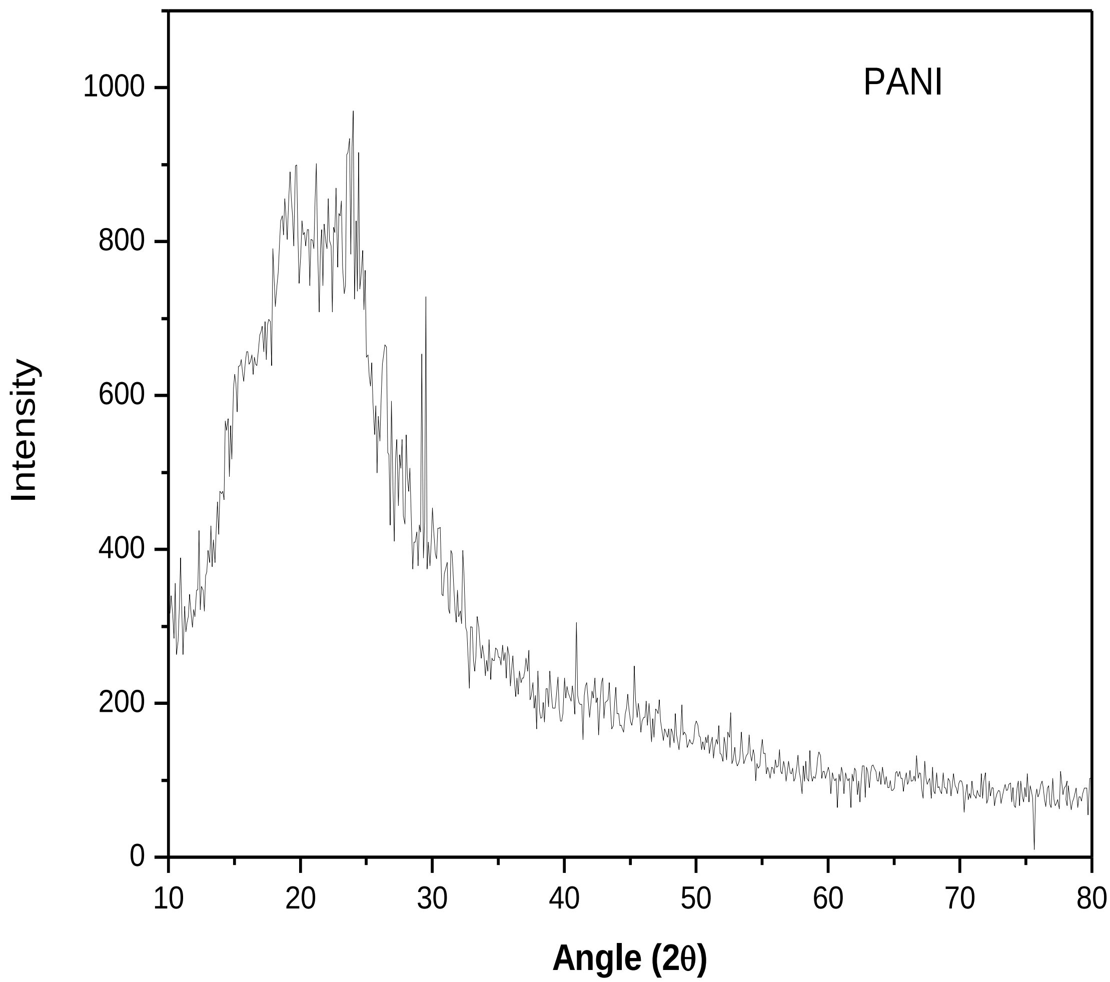

Fig. 1: X-ray Diffraction pattern of PANI

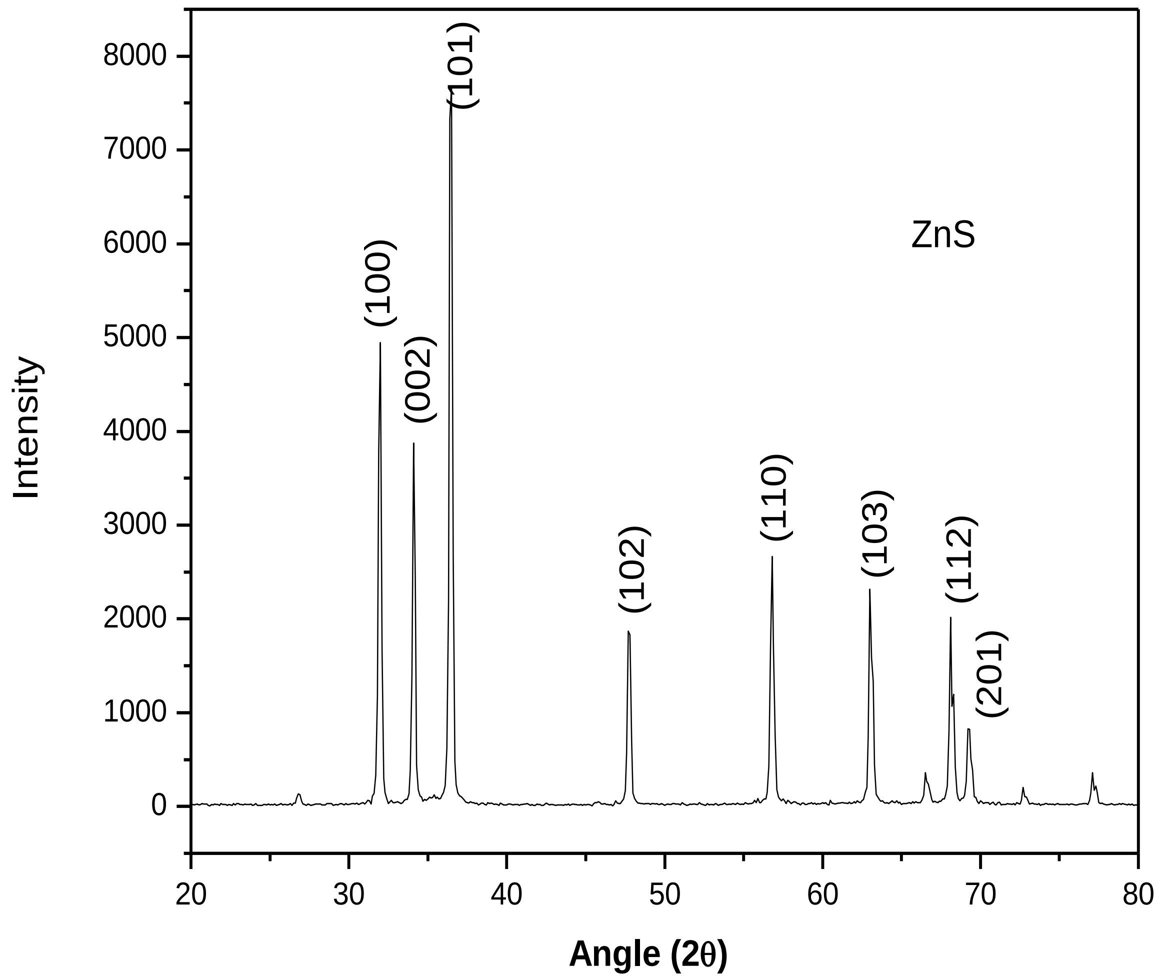

Fig. 2: X-ray Diffraction pattern of ZnS

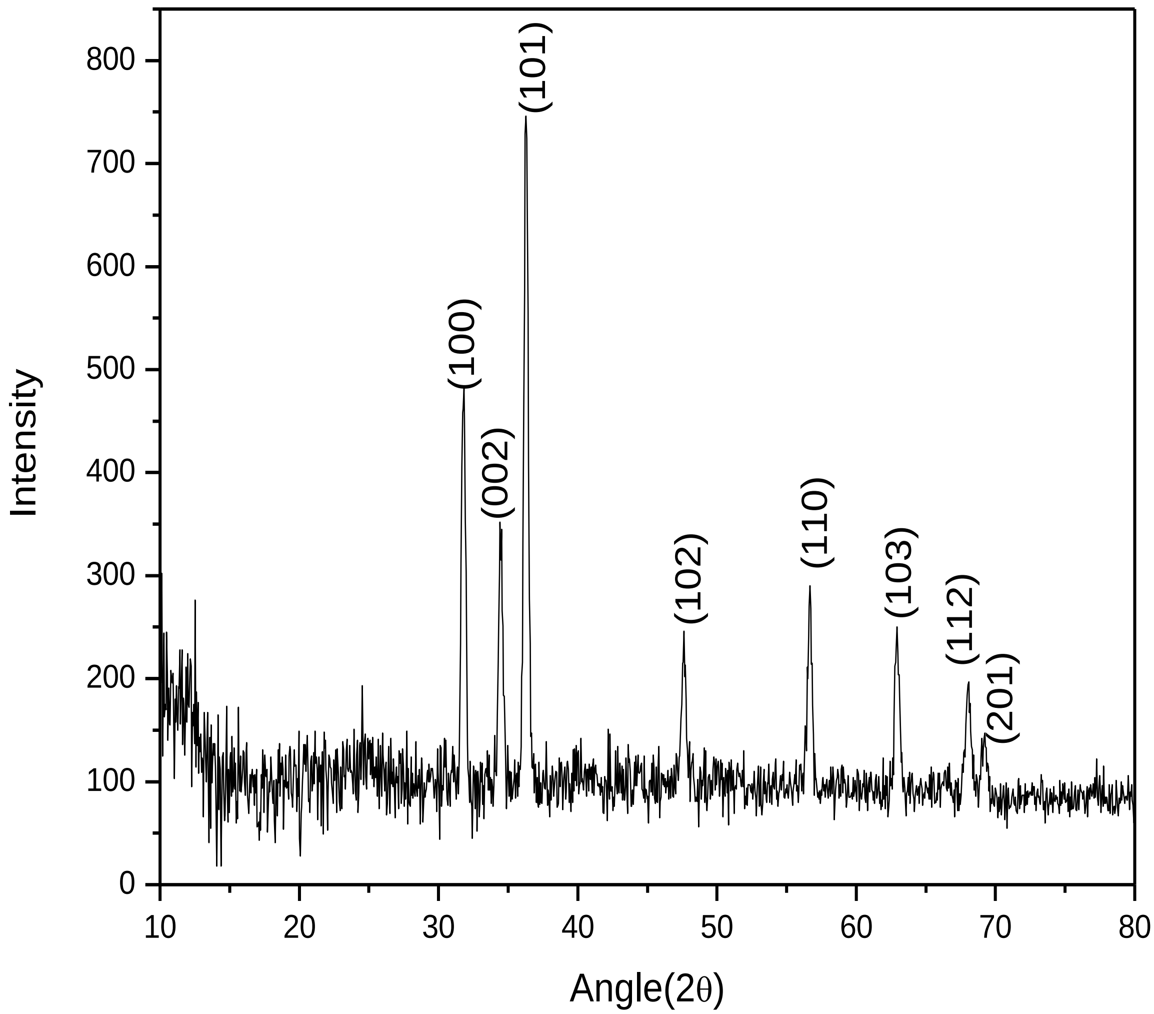

Fig. 3: X-ray Diffraction pattern of PANI on ZnS

(ii) Scanning Electron microscopy (SEM):-

The surface morphology of the material helps in the study of grain growth, orientation of the grains, compositional and topographical features present on the surface of the material. It is well known that different phases formed show different morphology when examined with the scanning electron microscope. From the scanning electron microscope it is possible to determine the compactness of the material, the particle size and shape etc.

The Scanning Electron micrographs obtained for Polyaniline on glass substrate and Polyaniline on ZnS thin film has been shown in fig..4 & 5, respectively. The results of the surface morphology are:

Polyaniline on ZnS shows a uniform morphology like pure Polyaniline film.

It shows some grain like structure due to the ZnS surface. The grains have become more regular and systematic for PANI on ZnS.

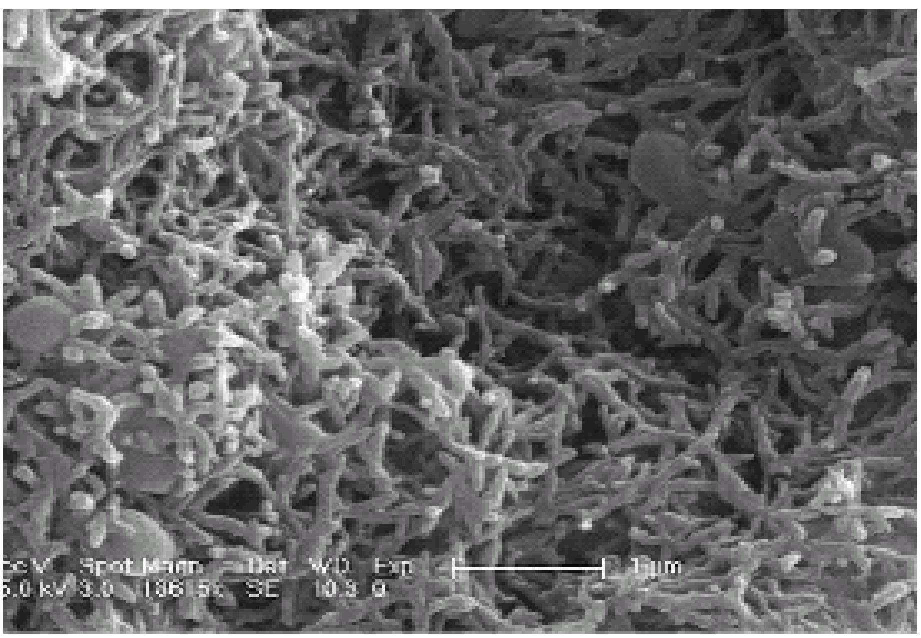

Figure 4: Scanning Electron Micrograph of PANI on glass

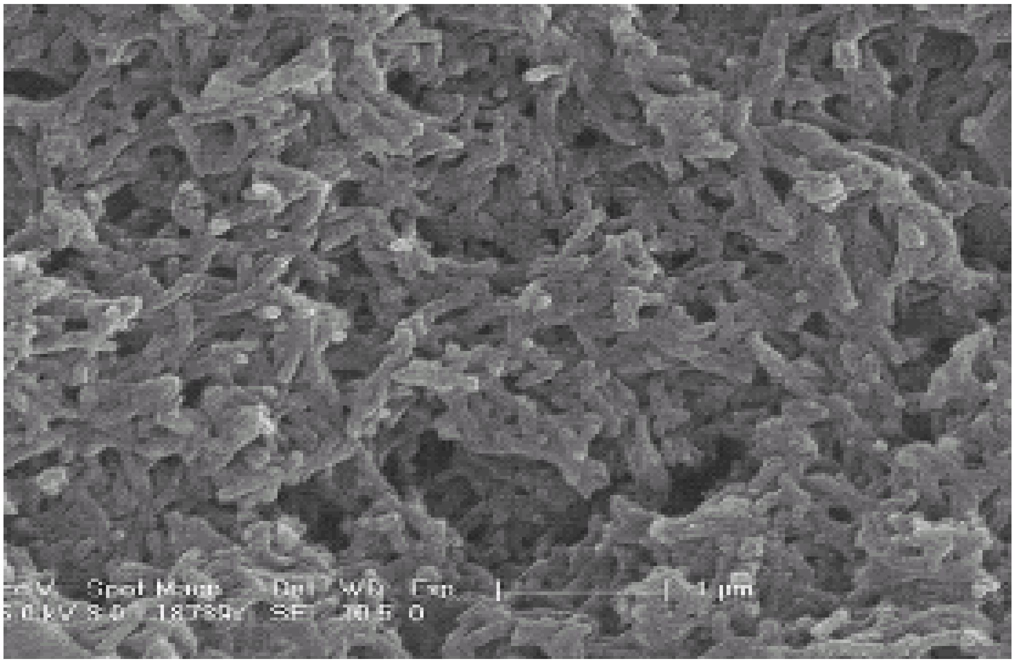

Figure 5. Scanning Electron Micrograph of PANI on ZnS

5. Result and Disscussion:-

The X-R-D of the sample gives the valuable information about the nature and structure of the film. The X-R-D pattern indicates the preferred orientation which is important part in structural characterization. In case of ZnS/glass the preferred crystallographic orientation is observed corresponding to (101) reflection, while in case of Pani/ZnS/glass same preferred orientation is observed but with modified intensity. The peaks observed in the XRD pattern shows that ZnS film has a polycrystalline hexagonal quartzite structure

The prepared films were subjected to scanning electron microscopy analysis to study surface morphology. The SEM studies of these thin films indicate a large increase in grain size up to 9 μ m, it is also observed that the substrate has a strong influence on the surface morphology of the film. Pani on Zns shows a uniform morphology similar to pure polyaniline film. It shows some grain like structure due to the ZnS surface. The grains have become more regular and systematic for pani on ZnS.

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