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SEM Studies of Polyaniline Thin Films Doped with Different Concentrations of KBr & $C_6H_3N_3O_7$

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ABSTRACT
Polyaniline has been the oldest among all the conducting polymers. 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. Polyaniline has rapidly become the subject of considerable interest for physicists, chemists and material scientists. In this paper we have carried out the Scanning Electron Microscopy characteristics of Polyaniline thin films doped with different concentrations (15% & 30%) of the dopants like Potassium Bromide and Picric Acid. The films has been prepared by using Vacuum Evaporation Technique and then characterized for SEM studies by using Scanning Electron Microscopy unit. The SEM study reveals that the grain size increases with the increase in the concentration of the above said dopants which in turn increases the crystallinity of the material. This behavior ensures its application in the optoelectronic devices.
Keywords: KBr, $C_6H_3N_3O_7$, Polyaniline (PANI), Scanning Electron Microscopy, Doping

I. INTRODUCTION
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) [1-2]. Polyanline is one of the oldest of conducting polymers and amongst the various conducting polymers Polyaniline (PANI) has rapidly become the subject of considerable interest for physicists, chemists and material scientists [3]. Among different conducting polymers, polyaniline are the most extensively studied material (Kumar et al 1996) [4-5]. 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, Gangopadhay et al 2001, Murugesan et al 2003) [6-9]. It has been shown that the conductivity of these heterogeneous system depends on a number of factors such as the concentration of conducting fillers, their shape, size, orientation and interaction between filler molecules and host matrix (Kryszewaski 1991, Brosseau et al 2001[10-11]. The geometrical shape of the dispersant governs the ability of conductive network formation which results in the large increase in the conductivity (Troung et al 1994) [12].
Conductive polymers generally exhibit poor electrical conductivity ($\sigma \leq 10^{-12}$ S/cm) in the virgin state and behave as insulators. These virgin polymers need to be treated with a suitable oxidizing or reducing agents to remarkably enhance their conductivities to the metallic region [13]. This phenomenon has been termed as "doping". Doping can be simply regarded as the insertion or ejection of electrons. The electrical, magnetic, electronic, structural and optical properties of the polymer get dramatically changed because of this doping process [14-15]. Doping of polymeric

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semiconductors is different from that in inorganic or conventional semiconductors. Inorganic semiconductors have three dimensional crystal lattice and on incorporation of specific dopant, n-type or p-type in ppm level, the lattice becomes only highly distorted.
The dopant so added is distributed along the specific crystal orientations in particular sites on repetitive basis. Whereas, doping of conducting polymer involves randon dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled chains and fibrils. The dopant concentrations may be as high as 50%. The addition of the dopants in the quasi 1-dimensional polymer material remarkably disturbs the order of the chain which in turn leads into the re-organisation of the polymeric material. Since doping is a reversible process due to which it can produce the original polymer either with small or no degradation of the polymeric material. Both doping and undoping process, involving dopant counter ions which stabilize the doped state, may be carried out chemically or electrochemically. Electrons are generated in the conduction band and holes are generated in the valence band by the doping of inorganic semiconductors.
In this paper we have reported the Scanning Electron Microscopic studies of Polyaniline thin films doped with different concentrations (15% and 30%) of the dopants like Potassium Bromide and Picric acid.

2. EXPERIMENTAL DETAILS

Sample Preparation

The structural properties of the films mainly depend upon deposition technique. Both science and technological, applications have been responsible for development of thin film technology. In the present work we have used vacuum deposition technique for the preparation of the samples.
KBr & $C_6H_3N_3O_7$ (Picric Acid), has been purchased from CDH company of chemicals with purity 99.9% and polyaniline was prepared by chemical method and obtained in powdered form. Doping of KBr & $C_6H_3N_3O_7$ with polyaniline according to stoichiometry (15% and 30% wt.) and the resultant solution of each (KBr & Picric acid) was stirred for 60 min and poured into 200 ml of 5-10% NaOH solution. The precipitate obtained was filtered, washed and dried. This powder was used for preparation of polymeric films by evaporation on glass substrate sufficiently at very high vacuum of the order of 10^{-6} torr. Thus the KBr and Picric acid doped Polyaniline thin films are formed. After doping thin film of doped polyaniline were prepared.

SEM Characterization of Pure and Doped Polyaniline

Surface morphology of Polyaniline (PANI) thin film has been studied by using Scanning Electron Microscope. The surface morphology of materials helps in the study of grain growth, orientation of the grains, compositions and topographical features present on the surface of the material. From SEM, it is possible to determine the compactness of the material, the particle size & shape etc.
The surface morphology of pure polyaniline is shown in the figure 1. This SEM shows that there is a formation of grains but they are not regular in arrangement and grain size differs within the shown region. This shows amorphous behavior. The grain size lies between .3 μ to 1.2 μ. Figure 2 shows the morphology of 15% KBr doped polyaniline. It shows a globular sponge like structure. In this SEM grain size increasing (in compression to pure PANI), which shows crystallinity increasing. From Figure 3 it is clear that the grain size of the SEM of 30% KBr doped polyaniline increases and arranges regular way. It means crystallinity is again increasing. The grain size varies 0.5 μ to 1.1 μ.
The morphology of 15% picric acid doped polyaniline is shown in figure 4, which shows that the grains is distributed in regular way but grain size is large in comparison to polyaniline. Figure 5 shows SEM of 30% picric acid doped polyaniline, which shows uniform distribution of grains and grain size is more regular. It is observed that the crystallinity is more in comparison to the SEM of KBr doped polyaniline.

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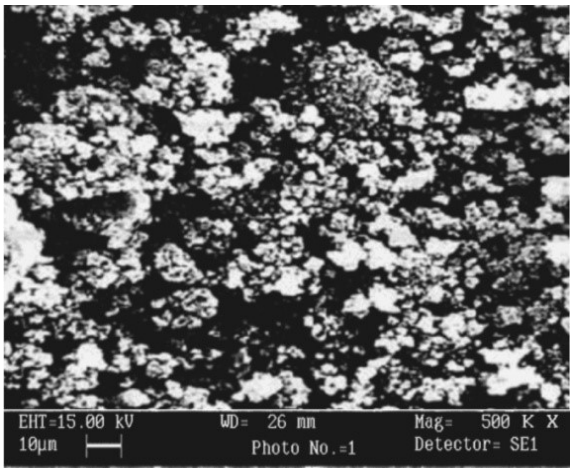

Fig. 1: SEM of PANI

Fig. 2: SEM of 15% KBr doped PANI

Fig. 3: SEM of 30% KBr doped PANI

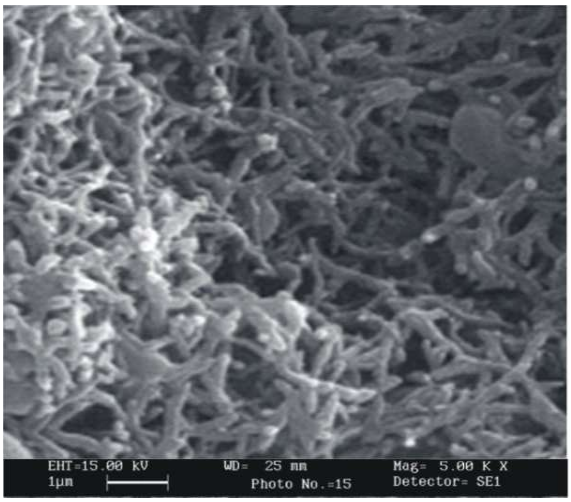

Fig 4: SEM of 15% Picric Acid doped PANI

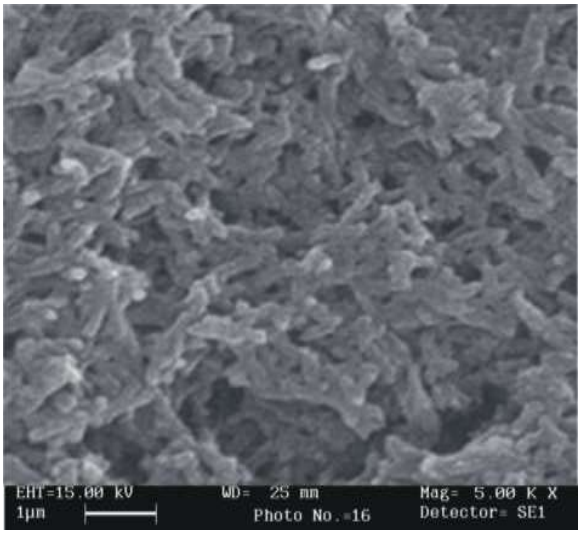

Fig 5: SEM of 30% Picric Acid doped PANI

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RESULTS & DISCUSSION

Surface morphology of the materials helps in the study of compositions and topographical features present on the surface of the material, orientation of the grains and growth in the grain size. Scanning Electron Microscopy assists to determine the compactness of the material, the particle size & shape etc. The Scanning Electron Microscopy studies of the prepared samples reveals that on doping the pure polyaniline thin films with different concentrations of the dopants like Potassium Bromide and Picric acid, the grain size increases with the increase in the concentration which in turn increases the crystallinity of the material and hence confirms its suitability in optoelectronic devices.

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