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Preparation and characterization of magnetic polymeric thin films

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Abstract

The revolution in information technology has led the scientists to look for advanced materials to cater for the growing capacity of data storage. Over the recent years, significant advances have been made in the development of materials, which possess smart and intelligent functions of the magnetic data storage and handling. These magnetic materials exhibit ferroelectric, ferrielectric and anti-ferroelectric properties. There have been successful attempts to prepare semiconducting conjugated polymers as potential materials, which has potential of being used as a base material. The magnetic properties of polyaniline are achieved by suitably doping the base material. We have developed a unique and novel method for preparation of polyaniline magnetic thin films by vapor deposition of magnetic polyaniline powder on various substrates. The characterization of thin films by optical absorption, SEM, X-ray are reported here. These studies suggest that vacuum deposited magnetic polyaniline thin films are suitable for magnetic data storage device fabrication.

Keywords: Polyaniline; Magnetic; Thin films; Data storage devices

1. Introduction

The need of miniaturization of electronic devices has led to the development of polymeric thin films magnetic devices. A great deal of attention has been focussed on the magnetic polymers that include polyaniline. The material is environmentally stable and solution processible. Although polyaniline has been known for years, their electronic uses have only been established recently. The structure and properties of this polymer have been widely studied and its feasibility as solid state devices for use as sensors, optoelectronic devices, energy storage devices, metallization of printed circuit boards, radiation shielding materials has been established. Polyaniline is prepared by various methods and is normally used as powder or pellet form. The nanocrystalline thin films of polyaniline have been proved to be suitable for fabrication of electronic devices.

2. Applications of magnetic polymeric thin films

Magnetic gyrator for phase shifters, insulators and amplifiers, magnetic memory devices disc storage, magnetic tapes and sheets, cards, electric field controlled FM resonance devices for usage as a switch or isolator, magnetically switched phase shifter, magnetically modulated piezoelectric devices, and magnetic non-linear optical devices

It is therefore, essential to study the magnetic properties go in to the details of feasibility on preparation of nanocrystalline magnetic polyaniline thin films and study the magnetic properties of these films. We have devised a completely dry process to prepare polyaniline thin films by vacuum evaporation of polyaniline powder on to suitable substrate. These films can be made magnetic by suitably doping the polyaniline powder during the synthesis. We hereby report the preparation and study of magnetic polyaniline vacuum deposited thin films for use in magnetic data storage applications.

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3. Experimentation

Preparation of undoped and Fe doped polyaniline nanocrystalline films was done in two steps. First, preparation of polymer and preparation of polymeric magnetic film on a substrate and second, preparation of nanocrystalline polymeric thin films on suitable substrates. A copolymer of aniline and formaldehyde was prepared by dissolving 10.5 gm of aniline in 12.5 ml of 10 M hydrochloric acid diluted with 11 ml distilled water. 12 ml of 25% formaldehyde solution was added to this solution, followed by addition of ferric chloride in a predetermined quality. The resultant solution 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 under a vacuum of 10^{-6} mmHg. Optical characterization of vacuum deposited magnetic polyaniline thin films was carried out using Hitachi UV-34OO spectrophotometer, Mossbauer spectroscopy, surface topography, X-ray diffraction analysis, electron spin resonance and electrically detected magnetic resonance were carried out. Since the thickness of the vacuum deposited films is of the order 1000 Å, it was required to carry out measurements at low voltages.

4. Results and discussion

Fig. 1 shows the optical UV-visible spectra of magnetic thin films, it can be seen that doping of polyaniline with Fe has remarkable effect on optical absorption spectra and shifting of peak.

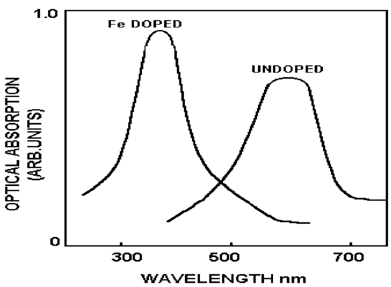

Fig. 1. Optical absorption of Fe doped polyaniline film.

Doping of polyaniline thin film by Fe induces crystallinity in the film as shown in Fig. 2. (SEM), which is a direct evidence of magnetizable non-crystalline domains. Fig. 3 shows ESR signals from vacuum, deposited polyaniline magnetic thin films. This signal also induces the EDMR signal that may be fitted with a Lorentzian. While the ESR signal is asymmetric as can be seen in Fig. 3, the asymmetry in the line shape can have different origins, possibly due to distribution of g-factor or spin diffusion related to a diverse conduction mechanism in polyaniline magnetic thin films due to polarons and bi-polarons. This may also give rise to typical ESR line shapes coming from structure of guest–host matrix structure arising out of Fe particles in otherwise semiconducting polyaniline base. EDMR signal is enhancing, i.e. $\Delta\sigma > 0$, as expected for conduction in polyaniline. The EDMR signals come from the peculiarities of the process of polaron hopping via paramagnetic sites. If we assume that in a magnetic polymeric thin films, the paramagnetic states are polarons and bi-polarons, there are various type of hopping processes associated with the various energy level occupied by the charged defects in polyaniline thin films, giving rise to the observed signals having a broad component. It is observed that for homogeneous resonance lines the linewidth of ESR/EDMR signals is inversely proportional to the spin–spin relaxation time. Thus for the broader component the relaxation time is most probably shorter than for the narrower line. For electric fields higher than 200 V/cm the conductivity is found to increase exponentially with the electric field, which is direct evidence of non-linearity in polyaniline thin films as reported earlier [1–3].

From the above results it can be concluded that the spectra show presence of dopant in polyaniline thin films which further reveal complete homogenization and paramagnetic behavior of the film. The Mossbauer spectroscopic analysis of Fe-doped polyaniline thin films were carried out and Mossbauer parameters were calculated from the graph which show isomeric shift 0.355 mm/s with respect to ∝-Fe, quadrupole splitting 0.693 mm/s and linewidth 0.505 mm/s (Fig. 4). The

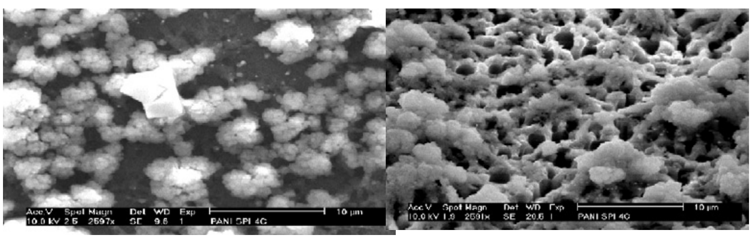

Fig. 2. Scanning electron micrograph of undoped and Fe doped polyaniline thin film.

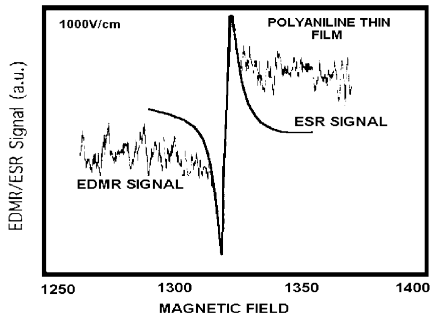

Fig. 3. ESR/EDMR signals.

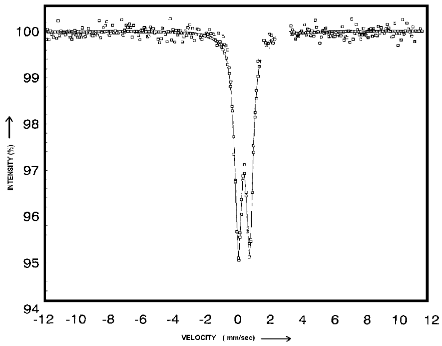

Fig. 4. Mossbauer spectra.

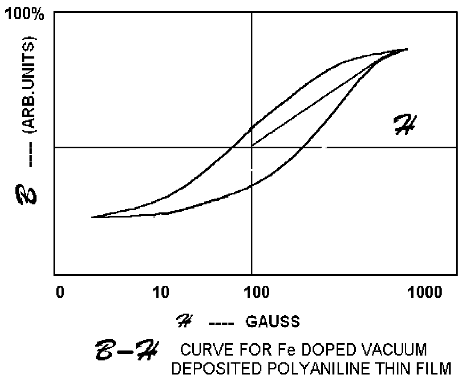

Fig. 5. $B-H$ curve.

$B-H$ curve also shows magnetic behavior of polyaniline thin films Fig. (5).

5. Conclusion

The feasibility of preparation of vacuum deposited magnetic nanocrystalline polyaniline thin films for device applications has been established. The optical absorption, ESR/EDMR study indicates the presence of free charge carrier in the magnetic thin films. The ESR studies and SEM study are indicative of presence of magnetizable domains in the thin films. These domains can be magnetized at low fields as indicated by $B-H$ curve. It can be concluded that vacuum deposited polyaniline thin films hold potential for being used as active magnetic devices for a wide variety of applications like storage media.

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