STRUCTURAL MORPHOLOGY AND DIELECTRIC PROPERTIES OF POLYANILINE-EMERALDINE BASE AND POLY METHYL METHACRYLATE THIN FILMS PREPARED BY SPIN COATING METHOD

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Abstract

Structural morphology, annealing behavior and dielectric properties of polyaniline–emeraldine base (Pani-EB) and poly methyl methacrylate (PMMA) thin films prepared by spin coating technique have been studied. MIM and MISM structures were used to investigate annealing and dielectric behavior. The XRD and AFM spectrum of as grown and annealed thin films indicates the amorphous nature. The observed amorphous phase, low loss, dielectric behavior and thermal stability even at high temperatures implies the feasibility of utilizing PMMA and Pani-EB thin films as gate dielectric insulator layer in organic thin film transistors which can find application in flat panel display.

1. Introduction

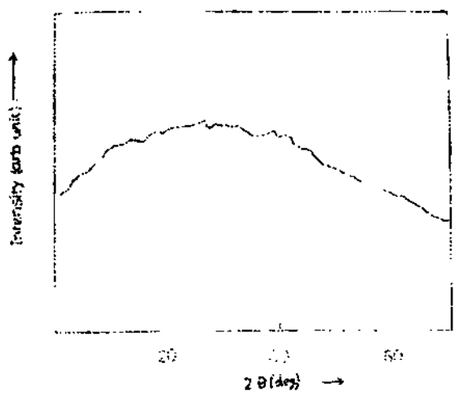
Polyaniline is one of the promising and useful polymer material due to its environmental stability and high thermal stability up to ~400 ^{0}C. It exists in four different forms: leucoemeraldine base (fully reduced, insulator); emeraldine base (half reduced-half oxidized, weak insulator); pernigraniline base (fully oxidized, weak insulator) and conducting emeraldine salt. Leucoemeraldine base or emeraldine base blended with poly methyl methacrylate can be used as an efficient dielectric insulator layer in organic thin film transistor where as pernigraline base and conducting emeraldine salt form can be used as a gate electrode in organic field effect transistors which can find application in liquid crystal flat panel displays, active matrix all organic emissive flat panel displays, etc[1-3]. The present work deals with the important basic properties such as structural morphology, annealing and dielectric properties of polyaniline emeraldine base and poly methyl methacrylate thin films prepared by spin coating technique.

2. Experimental

Metal-Insulator-Metal (MIM) and Metal-Insulator-Semiconductor (MISM) sandwich structures were used to study the dielectric properties. Glass micro slides cleaned by ultrasonic agitation and vapor degreasing methods and p type silicon wafers degreased with organic solvents such as trichloroethylene (TEC) and acetone followed by a rinse in deionized water (DI), boiled in nitric acid (HNO_3) for 10 minutes, dipped in dilute hydrofluoric (HF) for 10 sec and a rinse in DI water were used as substrates. In the MIM structure pure aluminium (99.99, Balzers) was thermally evaporated under a vacuum of 10^{-5} Torr to form the base metal electrode, middle polymer insulator layer was formed by depositing polyaniline–emeraldine base (or poly methyl methacrylate) by spin coating and finally aluminium was again evaporated over the polymer layer to form the top electrode. MISM structure was fabricated by thermal evaporation of aluminium metal of thickness 200nm above the polymer layer deposited over silicon wafer to form the top electrode and below the silicon wafer to form the bottom electrode. The dielectric properties such as annealing behavior; variation of capacitance with temperature and frequency; variation of dielectric constant with temperature and frequency; variation of dielectric loss with temperature and frequency; and variation of capacitance with voltage for different frequencies were studied by measuring capacitance (C) and loss ($\tan\delta$) using Hewlett-Packard LCR meter for the frequency range (10kHz – 10MHz).

3. Results and discussion

The X-ray diffraction spectrum of Pani-EB and PMMA films of thickness 200nm are shown in the figures 1&2. The absence of any prominent peaks in the spectrum indicates the amorphous nature.



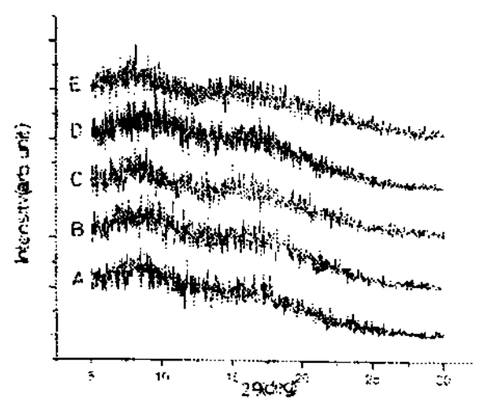
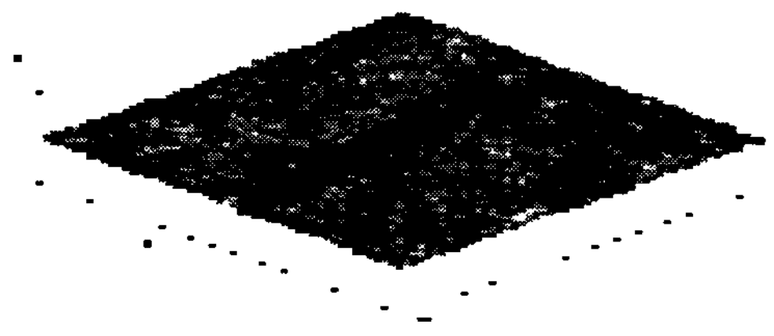
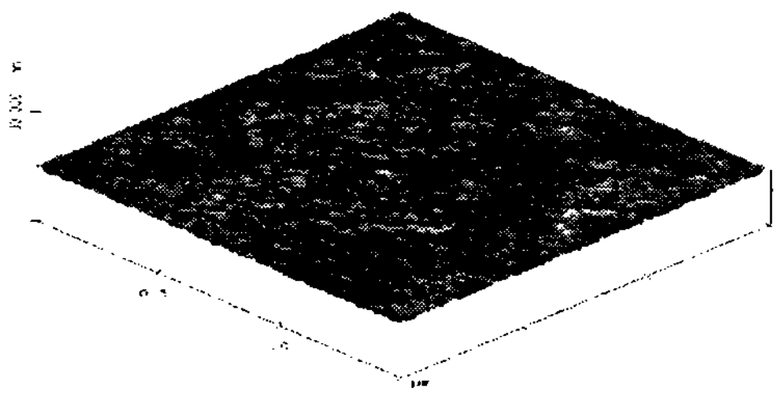


Figure 1 XRD of PaniEB. Figure 2 XRD of PMMA film:(A) as grown, (B) annealed at 230^{0}C,(C).250^{0}C, (D)270^{0}C &(E) 290^{0}C.

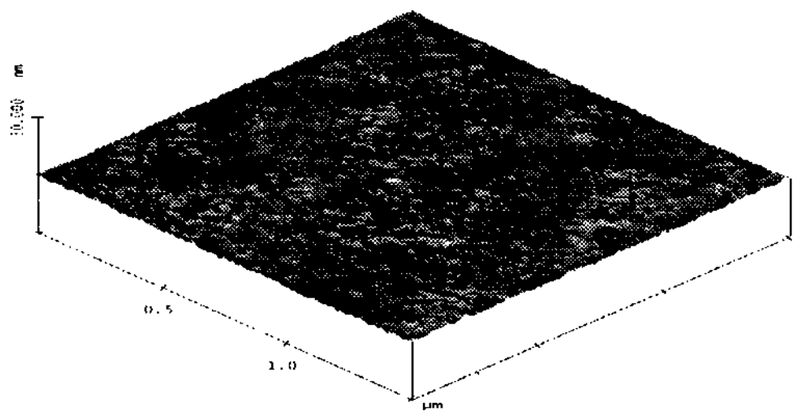
Figure 3 shows the atomic force micrographs (AFM) of as grown and annealed PMMA films of 200 nm. Both as grown and annealed films show the very



(A)



(B)



(C)

Figure 3 AFM of PMMA (A) as grown, (B) anneal ed at 230^0 C & (C) annealed at 290 ^{0}C.

smooth surface and amorphous nature. Surface roughness analysis of as grown and annealed PMMA films are given in the table1.

Figure 4 shows the annealing behavior for a pani-EB film of thickness 200 nm. Stable behavior is observed after 3 cycles of annealing for about 1 hour duration

Table 1 Roughness analysis of PMMA film

PMMA	Surface Area (μm)	RMS rough ness (nm)	Surface Area Difference
As grown	2.261	0.323	0.121
Annealed at 230^{0}C	2.265	0.257	0.152
Annealed at 290^{0}C	2.24	0.187	0.060

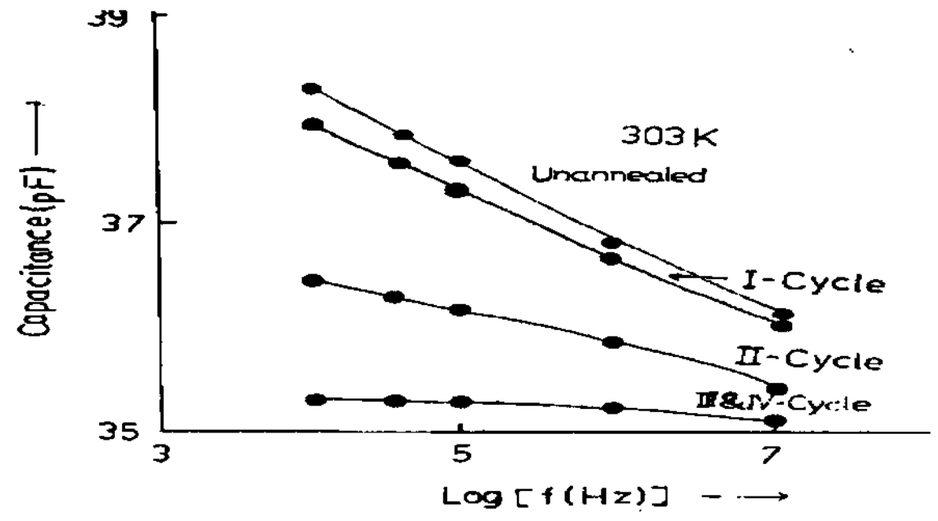


Figure 4 Annealing behavior of paniEB film

at T= 333K. Cycle after cycle, the defects are reduced gradually and each atom occupies a stable position in the interior of the film until the dielectric parameters attain a stable value[4]. Annealing of the film helps to control the structural organization of the polymer molecules in their solid state.

Generally the capacitance and dielectric constant are calculated from the formula

$$C = \varepsilon' \varepsilon_0 A/d \qquad \text{or}$$

$$\varepsilon' = Cd/A\,\varepsilon_0 \qquad (1)$$

where A is the area of the capacitor, d is the thickness of the dielectric layer, ε' is the dielectric constant of the material and ε_0 is the permittivity of free space (8.85×10^{-12} Fm^{-1}). Figure 5 shows the variation of capacitance with frequency for various temperatures for Pani-EB film. It is seen that the capacitance decreases in the low frequency range and attains a constant value in the high frequency range, which is the usual behavior observed in many polymer films[5,6]. The decrease of capacitance (C) with increase of frequency attributed to the trapping-detrapping of charge carriers due to gap states density in the amorphous film[7]. The increase of capacitance with the decrease of frequency in the lower frequency range can be approximately explained on the basis of charge carriers being blocked at the electrode[8]. In polymers, usually some charges exist, which can migrate for some distance through the polymer film on the application of the field. When such carriers are

impeded in their motion, either they become trapped in the materials, or on the interfaces, because they cannot be freely discharged or replaced at the electrodes. So space charge and macroscopic field distortion result. The space charge layer so formed should lead to a substantial increase in capacitance.

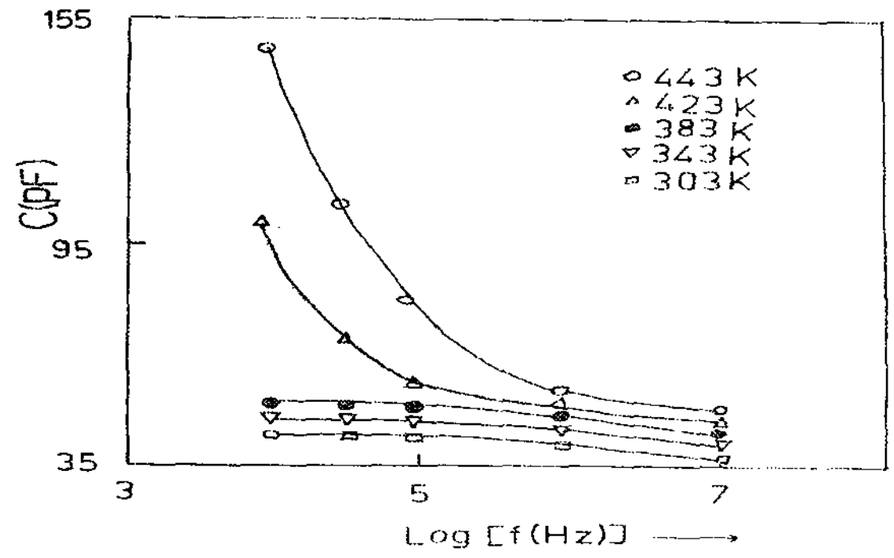


Figure 5 Variation of capacitance with frequency

The observed decrease of capacitance with increasing frequency is also attributed to the increasing inability of the dipoles to orient themselves in a rapidly varying electric field and slow release of charge carriers from relatively deep traps. Increase of capacitance above room temperature is partly due to the expansion of the lattice and partly due to the excitation of charge carriers present at the imperfection sites[9,5,6,8].

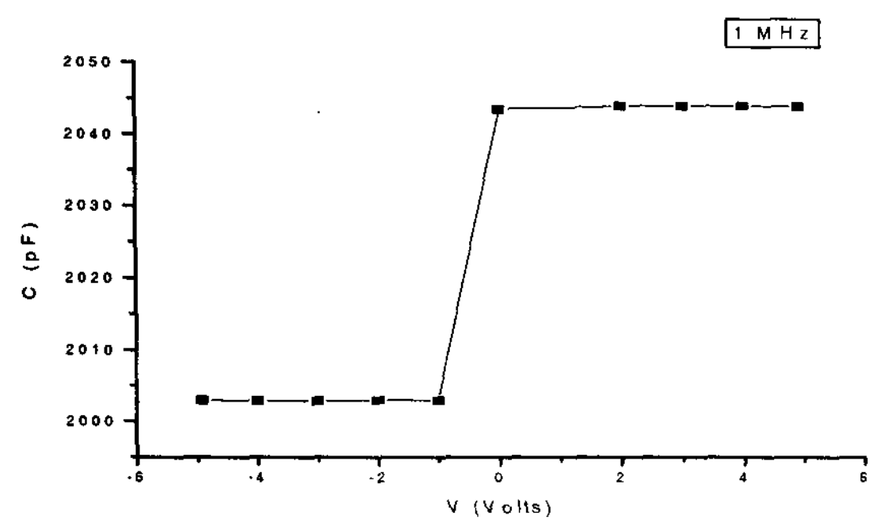


Figure 6 Variation of capacitance with voltage for PMMA film

The capacitance as a function of voltage (Figure 6) characteristics shows negligible hysteresis and flat band voltage. Similar C-V behavior was reported for hydrogenated amorphous carbon and ultra thin oxynitride films[10,11].

The variation of dielectric constant (ε') with frequency for various temperatures is shown in the figure 7. The observed decrease of dielectric constant with increase of frequency verifies the fact that, for polar materials, the initial value of ε' is high but as the frequency of the AC field is raised, the value of ε' begins to drop. The observed increase of dielectric constant with temperature may be assigned to the

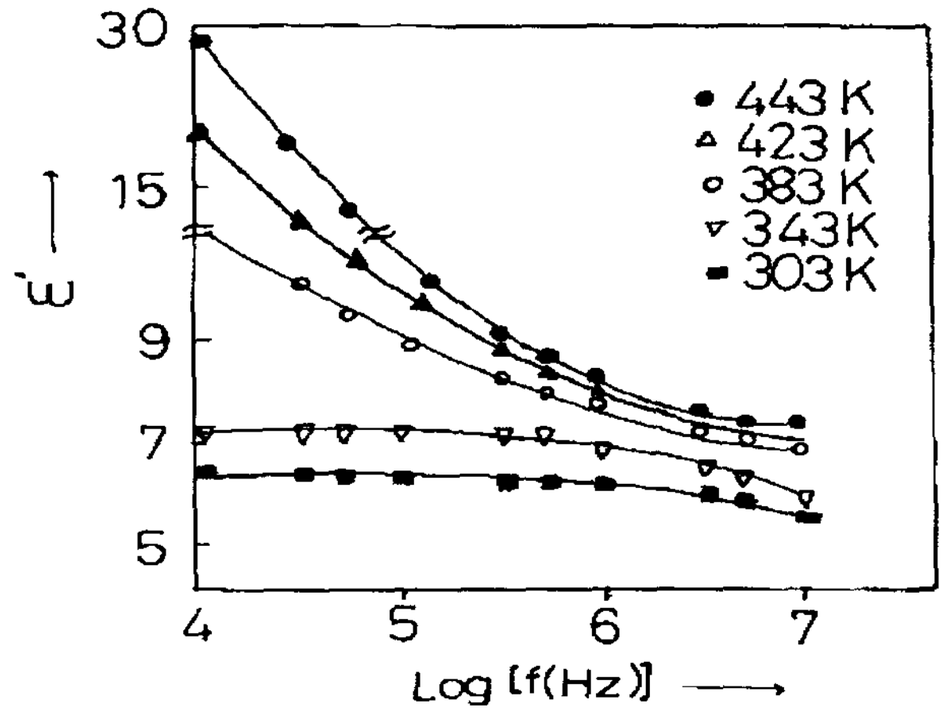


Figure 7 Variation of ε' with log f for Pani-EB

reasons such as changes in the intra and inter molecular interactions, increase in the degree of crystallinity and enhancement of polarization in which mobile ions and electrons may be involved[12,5,6]

Figure 8 shows the variation of dielectric loss (tanδ) with frequency and temperature.

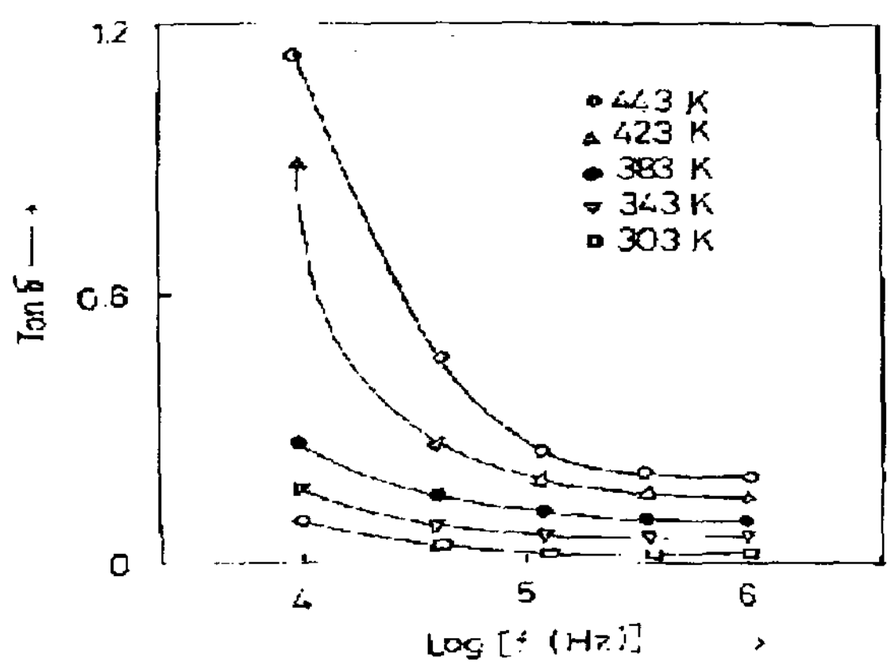


Figure 8 tanδ versus log f for Pani-EB film

The observed behavior can be explained by the following equations.

Dielectric loss $\Rightarrow \tan\delta = 1/\omega RC + \omega rC$

At high temperature (T), the value of R is low. So

$\tan\delta = 1/\omega RC \rightarrow$ is high

At low temperature (T), the value of R is high. So

$\tan\delta = 1/\omega RC \rightarrow$ is low.

The increase of loss factor at very low frequencies before the attainment of glass transition temperature (T_g) is due to dipole polarization. As the frequency increases the dipole polarization effect will tend to zero and the dielectric loss factor depends only on the electronic polarization. The magnitude of the loss factor increases with increase in temperature before the attainment of glass transition temperature (T_g). The dependence of crystallinity is usually observed at temperatures higher than the glass transition temperature of the amorphous regions[5,6,9]

By plotting capacitance against temperature (Figure not shown), the temperature coefficient of capacitance (TCC) is calculated from the relation,

$$TCC = 1/C\,(dC/dT) = \frac{1}{C1}\,\frac{(C_2 - C_1)}{(T_2 - T_1)}$$

Similarly by plotting permittivity against temperature (Figure not shown), the temperature coefficient of permittivity (TCP) is calculated from the relation

$$TCP = 1/\varepsilon\,(d\varepsilon/dT) = \frac{1}{\varepsilon_1}\,\frac{(\varepsilon_2 - \varepsilon_1)}{(T_2 - T_1)}$$

The linear expansion coefficient or the thickness expansion coefficient (α) is evaluated from the relation[13]

$$\alpha = TCC \sim TCP$$

The calculated value of TCC, TCP and α are given in the table 2.

Table 2 Values of TCC, TCP and α for various frequencies.

Film	Frequency (kHz)	TCC PPM/K	TCP PPM/K	α PPM/K
Pani-EB	10	33300	17100	16200
	100	6500	3000	3500
	1000	2800	2000	800

The predominantly amorphous nature observed for the polymer films eliminates the possibility of inhomogeneities responsible for the dielectric dispersion in these films. It may be concluded that the dielectric dispersion may be a bulk property of the polymers.

4. Conclusion

XRD and AFM spectrum indicates the amorphous nature of the films studied. The dielectric loss value was found to be minimum for the frequency range 10 kHz to 10 MHz. The low loss (leakage current) implies a large band-offset for electrons and holes. The annealed films show the stable dielectric properties. The decrease of capacitance value during the annealing cycle could be attributed to the rearrangement and orientation effects caused by polymer thermal annealing. The dielectric dispersion observed may be due to the bulk property of the polymers. The observed amorphous phase, dielectric behavior, thermal stability and low loss implies the feasibility of utilizing PMMA and Pani-EB and their blend as gate dielectric layer in OTFTs.

5. References

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