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Nano polymer films by fast dip coating method for field effect transistor applications

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Abstract

Nano Polyvinyl alcohol films are prepared by fast dip coating method. Cleaned glass plates are used as substrate to prepare the above said films. The thickness of the films are measured by capacitance method, weighing method and cross checked by electronic measuring instrument (Tesatronic-TTD 20). IR spectrum is used to identify the coated films. The coated films are identified by IR spectrum. No pits and pin holes are found on the surface. The XRD spectrum indicated the amorphous nature of the films studied. Aluminium/PVA/Aluminum sandwich structures are formed to study the dielectric and AC conduction behaviour. The capacitance and dielectric loss of the films are measured in the frequency range of 0.1 kHz to 100 kHz for various temperatures ranging from 290 K to 450 K. The observed increase of capacitance with the decrease of frequency in the lower frequency range can be assigned to charge carriers being blocked at the electrodes. The decrease of capacitance with increasing frequency is also attributed to the increasing inability of the dipoles to orient them selves in a rapidly varying electric field. The AC conductivity is found to vary according to the relation $\sigma_{ac} \; \alpha \; \omega^{n}$, where the value of n depends on temperature and frequency. The value of activation energy is found to be 0.0015 eV ~0.007 eV for various temperatures confirms the amorphous nature of the film.

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1. Introduction

Polymers are amorphous or semi-crystalline substances. In amorphous substances there are many localized charge carrier levels called trapping sites and the carrier mobility is very low. The transport mechanism in amorphous materials is more complicated than in crystalline materials, where a long range order exists. The dielectric properties of PVA are considered to be a good tool for studying the polarization as well as molecular relaxation mechanisms dealing with the dynamics of the mobile groups. Also, PVA is considered as an important polymer material due to its wide use in applications such as surgical devices, implantation, for a synthetic articulate cartilage in reconstructive point surgery, in electronics, fuel cell, optical waveguide sensors, humidity sensors, food packaging, drug delivery, production of polarizing sheets, holographic gratings and as dielectric layer in organic thin film transistors.[1-12]. In addition, PVA polymeric material may find several applications as tissue equivalent and as good insulator for organ preservation as well as pyroelectric detectors. Thus, the study of the structure and electrical properties is of particular interest in this report. To our knowledge there is no report on the physical properties of nano scale PVA films. In the present work an attempt has been made to study the growth, structure, dielectric and AC conduction properties of solution grown PVA nano scale thin films.

2. Experimental

Initially pure aluminium (99.99%) was evaporated at a pressure of $\approx 10^{-5}$ Torr from a helical filament by resistive heating onto pre-cleaned glass substrates through suitable masks to form the bottom electrode using vacuum coating unit. Polyvinyl alcohol was then deposited by a fast dip coating technique by isothermal immersion of the substrates into the polymer solution of a suitable concentration. The aluminium top electrode was then evaporated onto the polymer layer to complete the Al-PVA-Al structure. The thickness of the films were measured by weighing method, capacitance method and cross checked by electronic thickness measuring instrument (Tesatronic-TTD-20). The capacitance and loss values were measured by a LCR meter. The current - voltage (I-V) characteristics were studied by using a HP 5270A. Morphology and structural properties were studied by using XRD and SEM.

3. Results and discussion

Fig. 1 shows the infrared spectrum of PVA thin film of thickness 67 nm. The spectrum of PVA film found to be consistent with the previous reports in literatures for PVA film. The bands at 678 cm^{-1} and 751 cm^{-1} are assigned to out of plane O-H bending. The band at about 1246 cm^{-1} results from wagging vibration of C-H. The absorption band obtained at about 2924 cm^{-1} result from stretching of CH_2 group. The relatively broad and intense absorption observed at around 3429 cm^{-1} indicates the presence of bonded O-H stretching vibration.
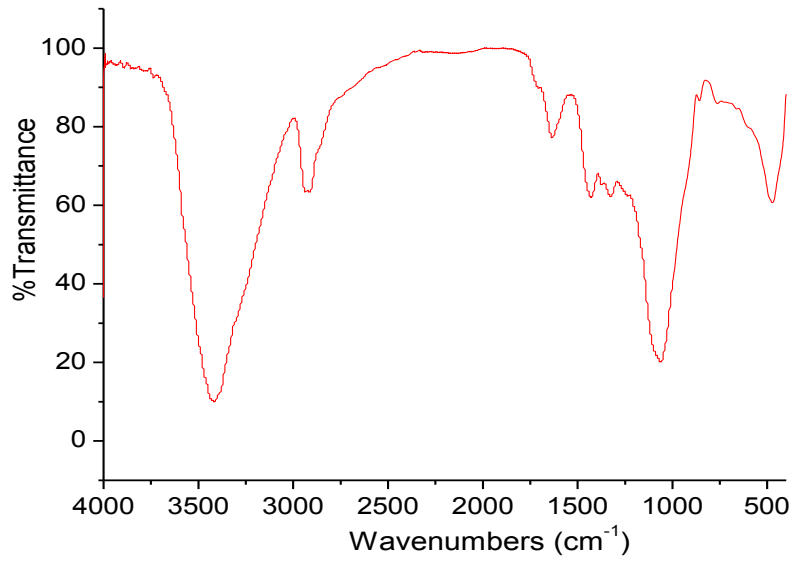
Fig. 1. IR spectrum of PVA film of thickness 67 nm

The x-ray diffraction spectra of PVA film of thickness 67 nm is as shown in the Fig.2. The x-ray diffraction pattern indicated the large diffraction maxima that decreases at large diffraction angles.
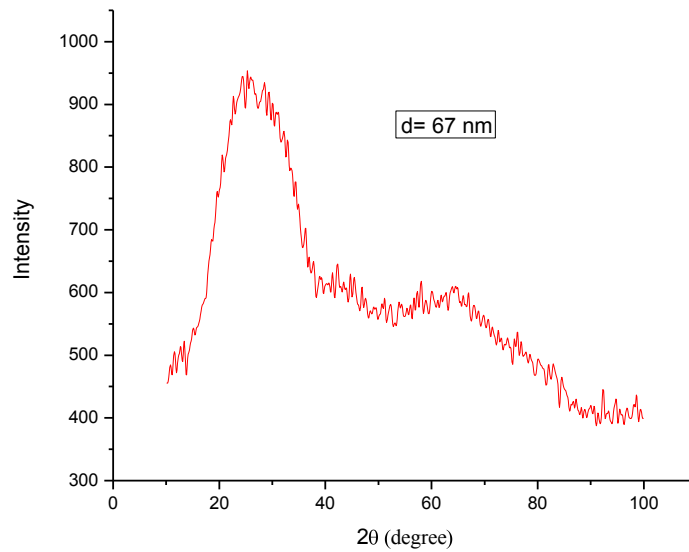

Fig. 2. XRD spectrum for PVA films of thickness 67nm

The first main maximum indicates the ordered packing of the polymer chains and the second maxima related to the effect of ordering inside the main chain. The absence of any intense peaks throughout the spectrum indicates the amorphous nature of the film. The scanning electron micrograph of PVA film of thickness 67nm is given in the figure 3. The surface of the PVA film appeared to be very smooth and uniform. No cracks and pin holes are observed. The SEM figure again reveal the amorphous nature of the film.
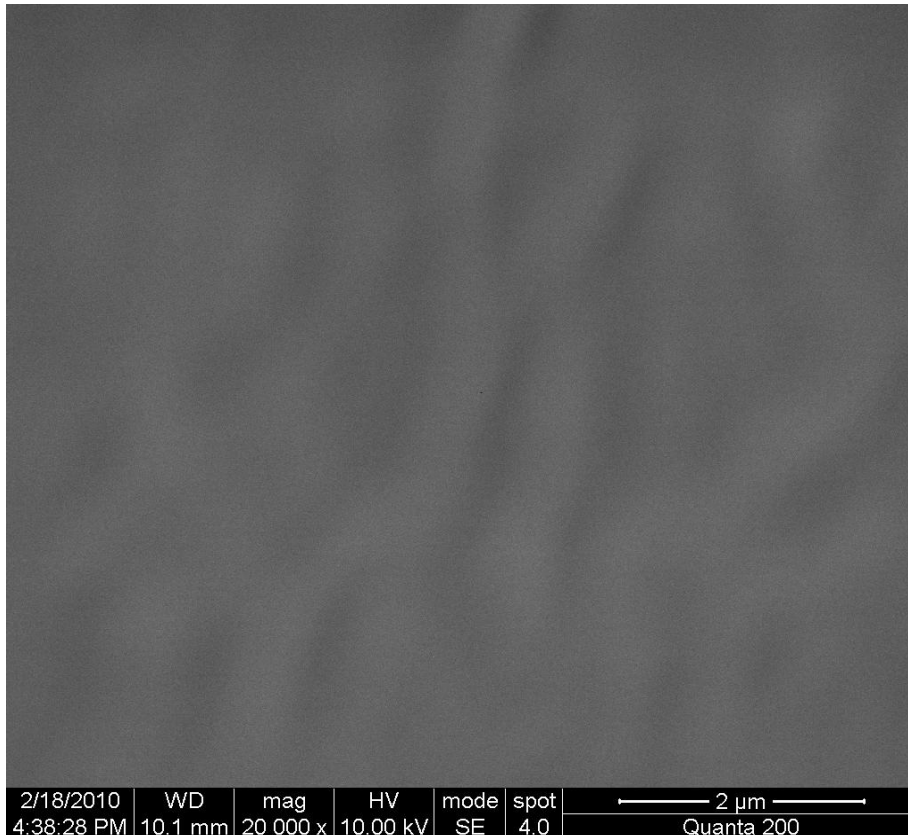

Fig.3. SEM Micrographs of PVA film of thickness 67nm

3.1 Dielectric properties

Fig.4 shows the variation of capacitance with frequency for PVA film of 67nm. It is seen that the capacitance decreases in the low frequency range and attains a constant value in the high frequency range, it is the usual behaviour observed in many dielectric films. The large increase in capacitance at lower frequencies with increase in temperature may be attributed to interfacial polarization [3,13]. The decrease of capacitance with increasing frequency is attributed to the increasing inability of the dipoles to orient themselves in a rapidly varying applied field.
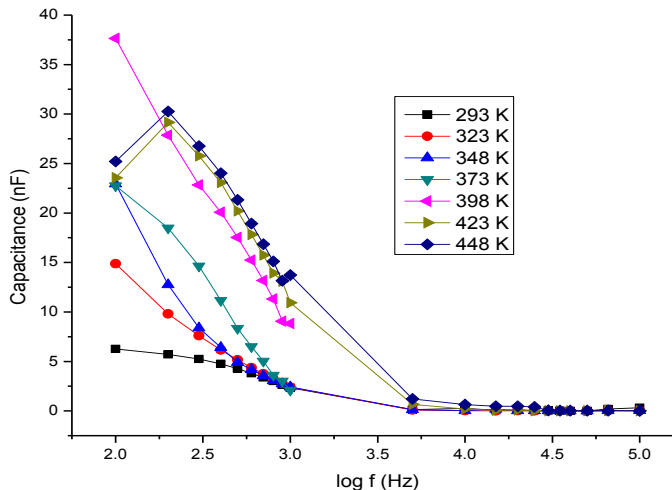
Fig.4. Capacitance Vs log frequency curve for PVA film of 67 nm.

Fig. **5** shows the frequency and temperature dependence of dielectric constant for a film of thickness 67 nm. The dielectric constant (ε') decreases with increases of frequency is verifying the fact that, for polar material (PVA), the initial value of ε' is high but as the frequency of the AC field is raised, the value of ε' begins to drop [14].
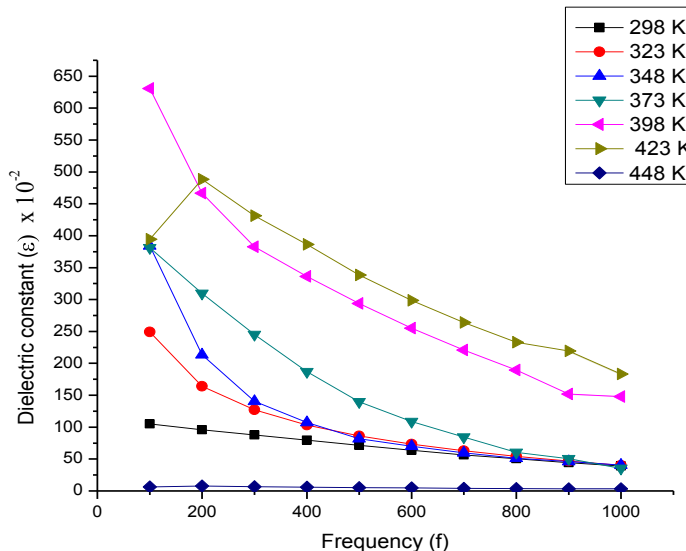

Fig. 5. Variation of dielectric constant with frequency for different temperatures.

The dielectric constant (ε') increases with the increase in temperature owing to the enhancement of polarization in these materials which the mobile ions and electrons may be involved [15,16]. The increase in ε' is also due to the increase in degree of crystallinity [17].
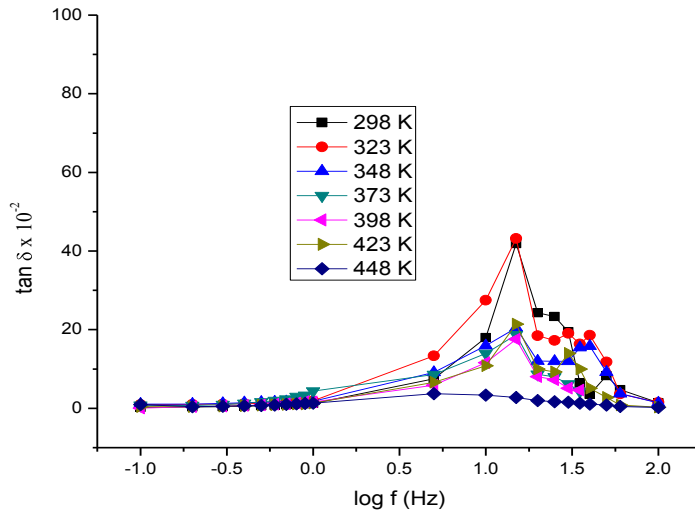

Fig.6. Dielectric loss Vs Log f for various temperatures.

The variation of dielectric loss (tan δ) with frequency for a film of thickness 67 nm at different temperatures is shown in Fig. 6. The value of tan δ increases a little with increase of frequency and temperature except for the temperature 298 K.
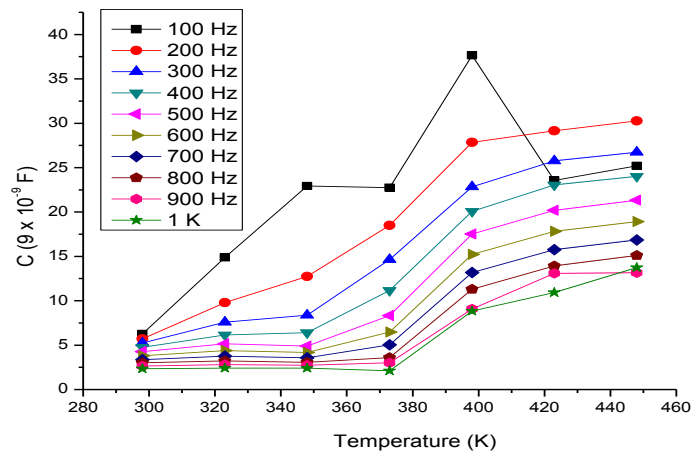
3.2 Temperature Coefficient of Capacitance

Fig.7. Temperature dependence of capacitance for various frequencies.

The temperature dependence of capacitance for various frequencies (100 Hz to 1 k) is shown in Fig. 7. The experimental curve exhibit a gradual rise in the capacitance with all temperatures. At higher temperature the variation of capacitance is more pronounced, while it is less pronounced in the low temperature region [18]. The temperature co-efficient of capacitance has been evaluated by using the given equation

$$TCC = \gamma_c = 1/C(dC/dT)$$

and the estimated TCC value has been found to be 84007 ppm/K for 1kHz.

3.3 Temperature coefficient of permittivity

The temperature dependence of permittivity for various frequencies (100 Hz to 1 k) is shown in Fig. 8. The experimental curve exhibit a gradual rise in the capacitance with all temperatures. The temperature co-efficient of permittivity TCP have been evaluated using the equation

$$TCP = \gamma_p = 1/\varepsilon'(d\varepsilon'/dT)$$

and it is found to be 84007 ppm/K for 1 kHz. The calculated values of TCC, TCP and α are given in table 1.
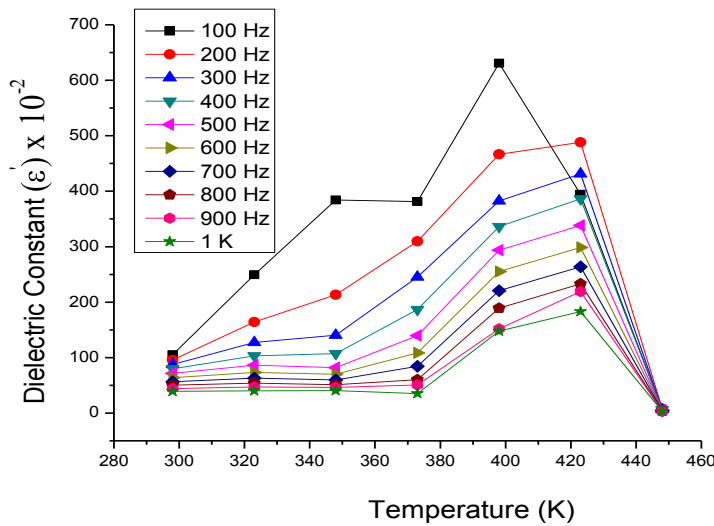
Fig. 8. Temperature dependence of dielectric constant for various frequencies

Table .1 Values of TCC, TCP and α

Frequency (Hz)	TCC x 10^4 (ppm/K)	TCP x10^4 (ppm/K)	α x10^4 (ppm/K)
200	1.1532846	1.1532841	0.005
400	1.5177217	1.5177210	0.007
600	3.4936416	3.4936413	0.003
800	5.7267301	5.7267291	0.01
1000	8.4007606	8.4007591	0.015

3.4 AC Conduction

The AC conductivity was calculated at different temperature using the equation

$$\sigma = \omega \, C_p \, \tan\delta \, d/A$$

Where σ - AC conductivity, ω -angular frequency, C_p – parallel equivalent capacitance, $\tan \delta$ - loss factor, d-thickness of the film, A- area of the polymer film. The double logarithmic plot of the dependence of AC conductivity on frequency (0.1 kHz to 100 kHz) at different temperatures is shown in Fig. 9.
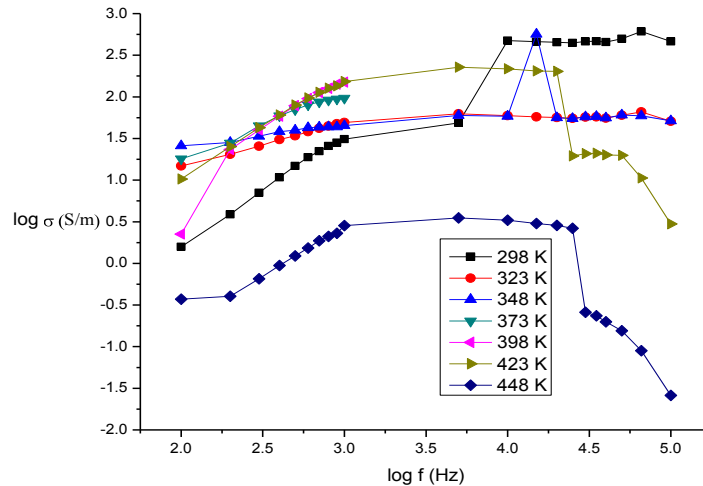

Fig.9. Log σ Vs Log f for various temperatures

AC conductivity is found to vary according to the relation $\sigma \, \alpha \, \omega^n$, where the value of n depends on temperature and frequency. From the figure 9 the value of n is around one. These values are in accordance with the theory of hopping conduction in amorphous materials [19,20]. The observed frequency dependence indicated that the mechanism responsible for the AC conduction could be a hopping one. The temperature dependence of conductance observed indicated the variable range hopping of charge carriers are responsible for conduction [20, 21]. When the charge carriers are localized there is no free motion of charge carriers and the conduction proceeds via the phonon assisted hopping of charge carriers between localized sites. Since the localized states have quantized energies extending over a certain range, activation energy is required for each hop.
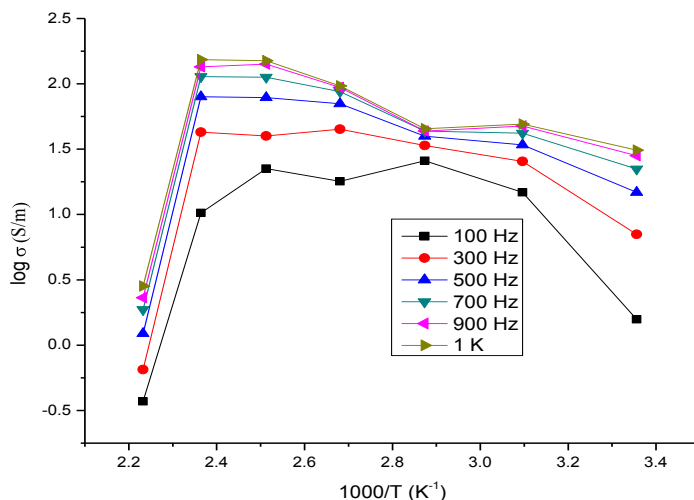
Fig.10. Log σ Vs 1000/T for different temperatures.

The activation energies have been calculated from the slopes of the log σ Vs (1000/T) plot as shown in the Fig.10. It is found to be around   0.007eV,   0.004 eV, 0.0027eV, 0.0021eV, 0.0018 eV, 0.0015 eV for the temperatures 298 K , 323 K, 348K, 373K, 398 K, 423 K,448 K respectively. The frequency dependence of conductivity together with low values of activation energy suggest that the conduction in nano scale PVA film is due to electronic hopping [21-24].

4. Conclusion

Polyvinyl alcohol nano scale thick films were prepared by a fast dip coating method. The XRD spectrum indicated the amorphous nature of the films studied.   SEM micrographs showed no pits and pin holes on the surface. The large increase in capacitance at lower frequencies with increase in temperature may be attributed to interfacial polarization. The observed decrease of dielectric capacitance with increasing frequency is attributed to the increasing inability of the dipoles to orient them selves in a rapidly varying applied electric field. The dielectric loss measurements indicated that the value of tan δ varies with temperature and frequency. The frequency dependence of conductivity together with low values of activation energy suggests that the conduction in nano scale PVA film is due to electronic hopping. The TCC and TCP values are very low and hence these thin film capacitance may be acting as effective passive devices in microelectronic circuits. The observed amorphous nature, dielectric and electrical behaviour indicated that nano scale PVA thin films could be used as an efficient dielectric layer in organic thin film transistors.

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