INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **35** (2002) 240–245 PII: S0022-3727(02)29462-0

Characterization of low dielectric constant polyaniline thin film synthesized by ac plasma polymerization technique

C Joseph Mathai[1], S Saravanan[1], M R Anantharaman[1,3], S Venkitachalam[2] and S Jayalekshmi[1,3]

[1] Department of Physics, Cochin University of Science and Technology, Cochin 682 022, Kerala, India

[2] Sci/Engr SG, PCM, VSSC, Trivandrum 695 022, Kerala, India

E-mail: mra@cusat.ac.in and sjr@cusat.ac.in

Received 4 October 2001
Published 22 January 2002
Online at stacks.iop.org/JPhysD/35/240

Abstract

Polyaniline thin films were prepared by ac plasma polymerization technique. Capacitance, dielectric loss, dielectric constant and ac conductivity of these films were investigated in the frequency range from 100 Hz to 1 MHz and in the temperature range from 300 to 373 K. Capacitance and dielectric loss decreased with frequency and increased with temperature. This type of behaviour was found to be in good agreement with an existing model. The ac conductivity $\sigma(\omega)$ was found to vary as ω^s with the index $s \leqslant 1$. Annealing of polyaniline thin films in high vacuum at 373 K for 1 h was found to reduce the dielectric loss. FTIR studies reveal that the aromatic ring is retained in the polyaniline thin films, which enhances the thermal stability of the polymer films.

1. Introduction

In recent years, the dielectric and electronic properties of polymeric and organic thin films have received a great deal of interest because of their importance in many advanced applications such as organic LEDs, sensors, rechargeable batteries, electroluminescent devices and as intermetallic dielectrics in ICs [1–5]. One of the fastest growing areas in the field of polymer thin film deposition are plasma assisted methods. Ac plasma polymerization is an inexpensive technique for the preparation of polymer thin films of varying thickness on a variety of substrates from almost any organic vapour. The polymers formed with the assistance of plasma are different from those formed by other conventional techniques [6, 7]. The properties of these films can be tailored according to requirements by varying the deposition parameters like pressure, applied current, monomer flow rate and time of polymerization. Pinhole free, chemically inert and thermally stable polymer thin films can be deposited by employing plasma polymerization technique [8].

Electronic and photonic properties of polyaniline have attracted considerable scientific interest due to its potential applications. Chemical methods and electrochemical polymerization of aniline on metallic electrodes is a common method for the preparation of polyaniline thin films. Many researchers [9–12], including Epstein and co-workers [13–16] and Kahol and co-workers [17, 18], have prepared polyaniline by chemical methods and have carried out dielectric studies in the microwave region. While plasma polymerization technique has been employed for preparing polyaniline thin films, reports on the electrical properties of these films are scanty [19–21]. We report here the preparation of polyaniline thin films by ac plasma polymerization technique. The investigation carried out on the dielectric properties and ac conductivity of these films is also discussed. Apart from the preparation of low dielectric constant thin films, one of the objectives of this paper is to explore the possibility of retaining the aromatic ring in the plasma polymerized aniline thin films. Retention of the aromatic ring in the deposited films enhances the thermal stability, which is essential for

[3] Authors to whom correspondence should be addressed.

applications such as low k intermetallic dielectrics [22] and gas separation membranes [23].

The shrinking design of ultralarge-scale integration (ULSI) circuits has increased the interconnection delay time caused by parasitic capacitance of the interconnects. In order to reduce the parasitic capacitance of interconnects, low dielectric constant materials should be used [24]. Low dielectric constant materials lower the RC time constants between interconnects, thus improving the overall IC speeds. In addition to the low dielectric value, the interconnect dielectrics must also satisfy a number of other criteria, so that they can be of use in various microelectronic applications. One important criterion is thermal stability [25, 26]. These materials should withstand the high temperature material processing imposed by IC fabrication technology.

2. Experimental

Ac plasma polymerization technique was employed for deposition of polyaniline thin films. The experimental setup is as shown in figure 1. It consists of two parallely placed electrodes, each of diameter 0.23 m and thickness 2×10^{-3} m, placed 0.05 m apart. Ultrasonically cleaned glass substrates, some of them precoated with Al electrode, were placed on the lower stainless steel electrode for polymer thin film deposition. The glow discharge chamber was evacuated and monomer aniline was injected in between the electrodes by means of a sprayer at a monomer vapour pressure of 0.2 torr. Discharge was obtained between the electrodes by applying a low frequency (50 Hz), high ac voltage (500–800 V) controlled by current in the range of 40–70 mA. The conditions for depositing plasma polymer films on substrates were standardized and optimized.

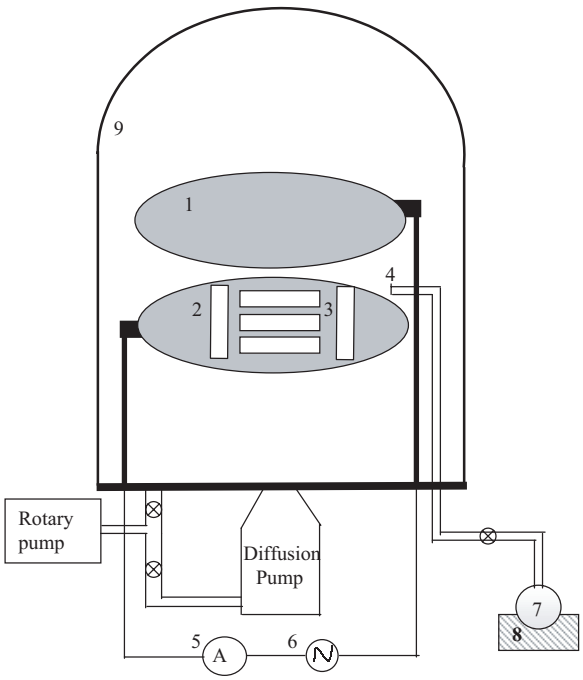

Figure 1. Ac plasma polymerization setup. 1, 2: stainless steel electrodes; 3: substrates; 4: sprayer; 5: ammeter to control current; 6: ac power supply; 7: monomer holder; 8: monomer heater; 9: glass bell jar.

Polymer thin films were grown under optimum conditions on the substrates kept on the lower electrode. These polymer coated substrates were then transferred with appropriate masks into a conventional metal coating unit for coating the second Al electrode under a pressure of 7×10^{-5} torr. These films were in the form of metal/polymer/metal of cross-sectional area 2.5×10^{-5} m^2. The thickness of the polymer films was measured by interferometric techniques and the thickness values lie in the range of 1200–2000 Å.

For dielectric and ac conductivity studies, these sandwich samples were placed in a home-built conductivity cell in which the temperature could be varied from room temperature to 373 K by a digital temperature controller, and the temperature was measured by an Fe–K thermocouple kept on the sample. Capacitance and dielectric loss were measured by an HP4192A Impedance Analyzer in the frequency range from 100 Hz to 1 MHz and in the temperature range of 300–373 K. Dielectric constant was evaluated from known values of capacitance, thickness and area of the sample. Ac conductivity was then obtained from the measured dielectric loss, dielectric constant and frequency using the relation $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta$. All the measurements were carried out under dynamic vacuum. The data acquisition and analysis was completely automated by employing the LabVIEW software (National Instruments).

3. Results and discussion

3.1. FTIR analysis

Figure 2 shows the FTIR spectrum of monomer aniline and plasma polymerized aniline. Most of the infrared absorption features characteristic of the monomer aniline are retained during plasma polymerization, although the peaks become broader, which is consistent with the highly disordered nature of plasma polymers. The polyaniline spectra show peaks at 1600, 1500 and 1450 cm^{-1}, indicating that the aromatic ring is retained in polymer thin films [27]. A peak at 3020 cm^{-1} is due to C–H stretch. N–H vibration is observed at 3370 cm^{-1}. Primary aromatic amine C–N stretch is

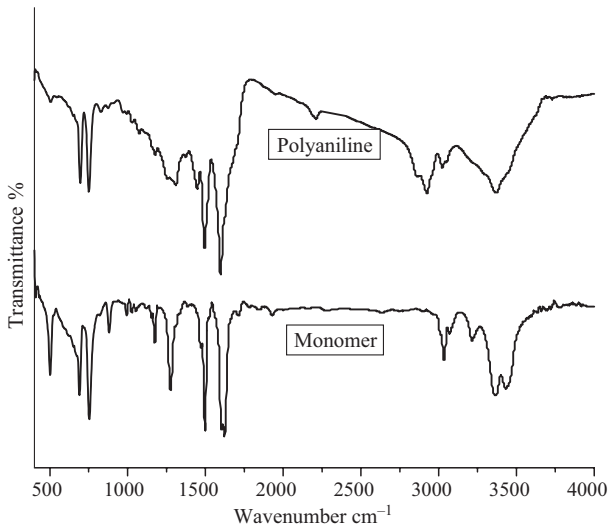

Figure 2. FTIR spectrum of monomer aniline and plasma polymerized aniline.

observed at 1310 and 1250 cm^{-1}. Substituted benzene peaks are observed at 750 and 694 cm^{-1}. Since the aromatic ring is retained in polyaniline thin films, thermal stability is enhanced [25].

3.2. Capacitance and dielectric loss as a function of frequency and temperature

The capacitance of the plasma polymerized aniline thin film measured as a function of frequency at different temperatures is shown in figure 3. From figure 3 it is clear that the capacitance is frequency dependent at high temperatures and low frequencies, approaching a constant value at high frequencies at all the measured temperatures. This type of behaviour can be adequately explained in terms of an equivalent circuit model proposed by Goswami and Goswami [28]. In this model the capacitor system is assumed to comprise a frequency independent capacitive element C' in parallel with a discrete temperature resistive element R, both in series with a constant low value resistance r. According to this model, the measured series capacitance C_s is given by

$$C_s = C' + \frac{1}{\omega^2 R^2 C'} \tag{1}$$

and loss tangent is given by

$$\tan\delta = \frac{(1 + r/R)}{\omega R C'} + \omega r C' \tag{2}$$

where ω is angular frequency. The temperature dependence of the model is represented by a thermally activated process given by

$$R = R_0 \exp\left(\frac{\Delta E}{kT}\right) \tag{3}$$

where R_0 is a constant and ΔE is activation energy.

Equation (1) predicts that C_s should decrease with increasing ω, and at high frequency C_s should fall to a constant value C' for all temperatures. Equation (1) also predicts that, for any given frequency, C_s will increase with temperature because of the decreasing value of R. All these effects are clearly observed in figures 3 and 4. The expression for $\tan\delta$ according to equation (2) predicts a decrease in $\tan\delta$ with increasing ω, where the term ω^{-1} is dominant for lower frequencies. It is then followed by a loss minimum at $\omega_{min} \cong 1/C'(rR)^{1/2}$ and finally increases with ω above ω_{min}, where the term ω is dominant. The variation of $\tan\delta$ as a function of frequency is shown in figure 5. As predicted by equation (2), $\tan\delta$ decreases with increasing frequency until a loss minimum is observed and thereafter it increases with increase in frequency. The increase in $\tan\delta$ with temperature shown in figure 6 is also consistent with equation (2) as the ω^{-1} term becomes dominant because of the decreasing value of R with temperature.

3.3. Dielectric constant as a function of frequency and temperature

The dielectric constant of plasma polymerized aniline thin films has been evaluated from the capacitance measurements given by the equation

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{4}$$

where C is the observed capacitance, d the thickness of the film, A the area of the film and ε_0 the permittivity of free space.

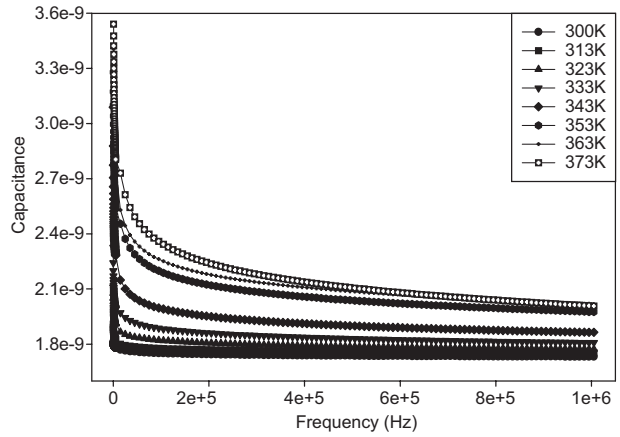

Figure 3. Capacitance of plasma polymerized aniline thin film of thickness 1200 Å as a function of frequency at different temperatures.

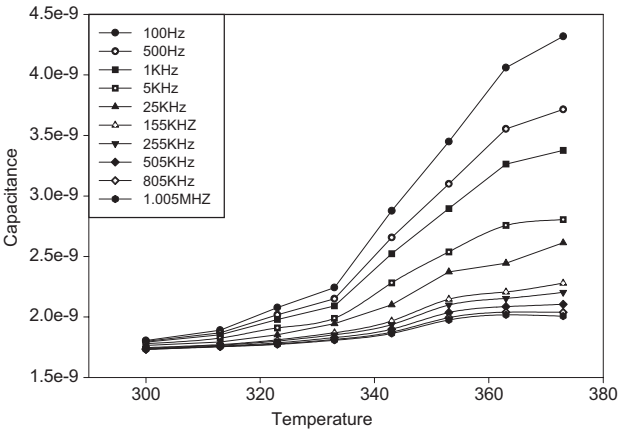

Figure 4. Dependence of capacitance of polyaniline thin film of thickness 1200 Å as a function of temperature at different frequencies.

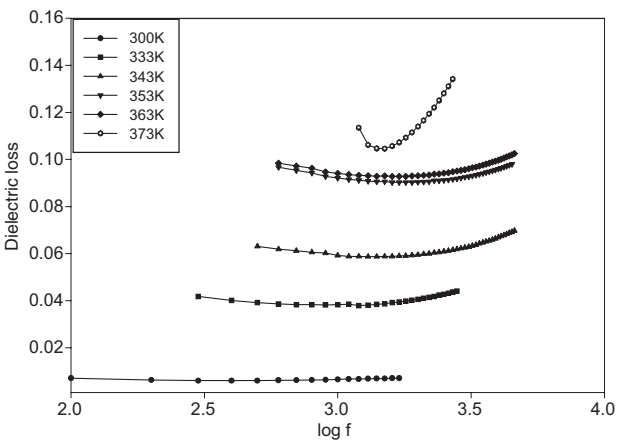

Figure 5. Dielectric loss of polyaniline thin film of thickness 1500 Å as a function of frequency at different temperatures.

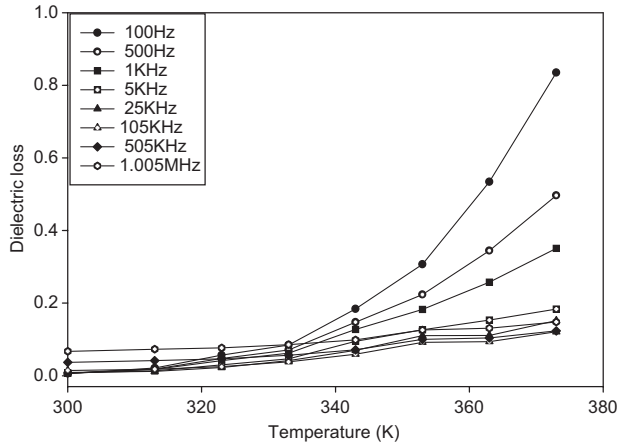

Figure 6. Dielectric loss of polyaniline thin film of thickness 1200 Å as a function of temperature at different frequencies.

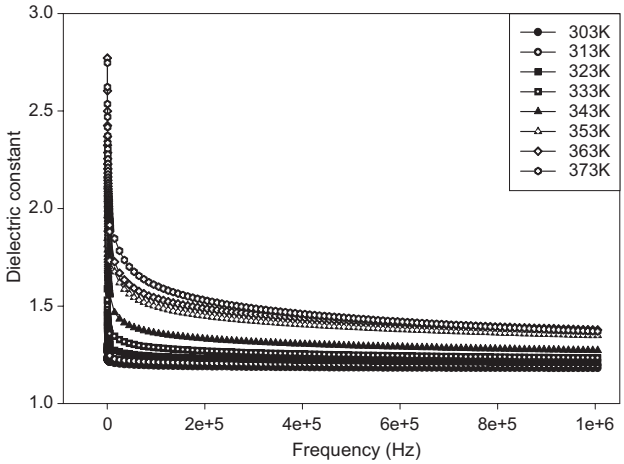

Figure 7. Dielectric constant of polyaniline thin film of thickness 1200 Å as a function of frequency at different temperatures.

The ε values are obtained in the frequency range from 100 Hz to 1 MHz at different temperatures. They are plotted as a function of frequency at different temperatures as shown in figure 7. It is found that in the whole frequency and temperature range scanned, the dielectric constant lies between 2.9 and 1.18, which is considerably low. The observed frequency dependence of the dielectric constant is due to the interfacial polarization, which is usually observed in sandwich type configurations. This type of low dielectric constant materials, when used as intermetallic dielectrics, reduces the *RC* time delay considerably in microelectronic circuits [24].

The time delay associated with interconnection depends on two factors, one of which is due to the resistance of the interconnections and the other to the capacitance associated with the dielectric media. A simple first order model has been developed to estimate the interconnection *RC* delay time [29]. *RC* delay can be calculated by the formulae

$$RC = 2\rho k\varepsilon_0 \left\{ \frac{4L^2}{P^2} + \frac{L^2}{T^2} \right\} \tag{5}$$

where ρ is the resistivity, L the length of the interconnection, T the metal thickness, k the dielectric constant, ε_0 the permittivity of air and $P = W + S$ (W and S represent metal width and the space between metals).

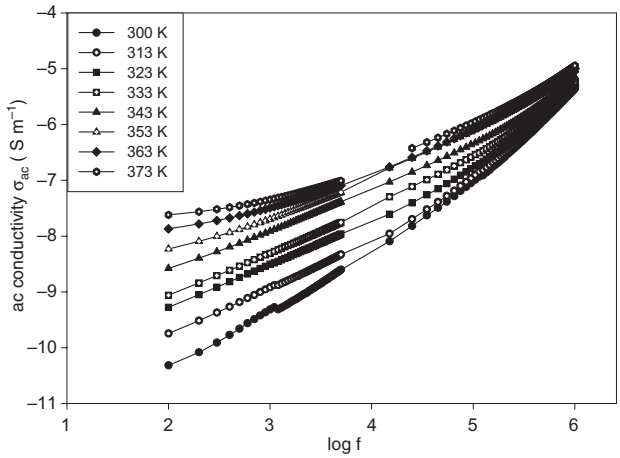

Figure 8. Ac conductivity of polyaniline thin film of thickness 1200 Å as a function of frequency at different temperatures.

The dielectric constant of the plasma polymerized aniline thin film at 1 MHz is found to be 1.18. According to equation (5), it is found that the substitution of SiO_2 ($k = 4$) with polyaniline of dielectric constant $k = 1.18$ will reduce *RC* delay by about 70%. However, replacement of Al by Cu will decrease *RC* delay by approximately 35% [5].

3.4. Ac conductivity as a function of frequency and temperature

The ac conductivity σ_{ac} as a function of frequency at different temperatures of ac plasma polymerized aniline thin film is shown in figure 8. It is found that σ_{ac} increases as frequency increases, with a higher slope in the high frequency regions (>10 kHz) for all the temperatures scanned. It is also observed that σ_{ac} increases more in the low frequency region (<10 KHz). This type of behaviour can be explained by the relation [30]

$$\sigma(\omega) \alpha\, \omega^n \tag{6}$$

where ω is the angular frequency and n is the index that is used to understand the type of conduction/relaxation mechanism dominant in amorphous materials.

The values of n determined from figure 8 are found to lie between 0.4 and 1 for low frequencies (<10 kHz). The value of n at lower frequency is in accordance with the theory of hopping conduction in amorphous materials [31]. The observed frequency dependence reveals that the mechanism responsible for ac conduction at low frequencies could be due to hopping [32, 33].

Figure 9 shows the variation of ac conductivity with temperatures at different frequencies. Activation energies were determined from these plots. It is found that the activation energies (0.334–0.056 eV) are low throughout the whole temperature and frequency range scanned. This strong dependence of conductivity on frequency and the low activation energies of the carriers are indicative of a hopping conduction mechanism in plasma polymerized aniline thin films. The above observations indicate that at low temperatures (around room temperature) the conduction mechanism is

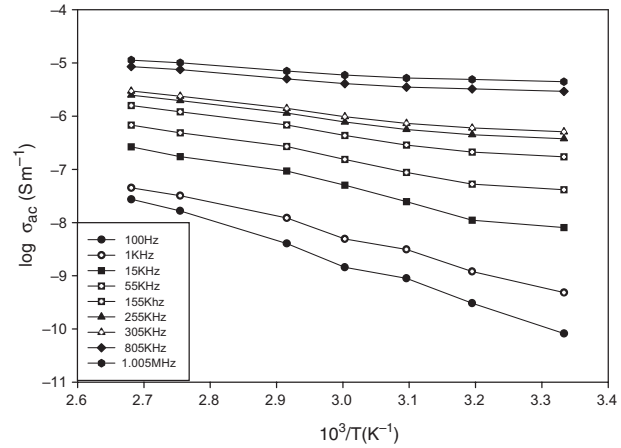

Figure 9. Ac conductivity of polyaniline thin film of thickness 1200 Å as a function of temperature at different frequencies.

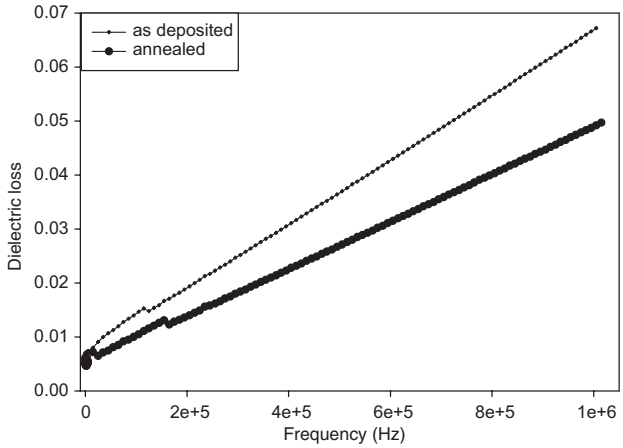

Figure 10. Dielectric loss of as-deposited and annealed (373 K for 1 h) polyaniline thin film of thickness 1200 Å.

dominated by the hopping of carriers between localized states, and at high temperatures it is due to the movements of thermally excited carriers from energy levels within the bandgap [34].

3.5. Effect of annealing on dielectric loss

The most important factors preventing the widespread application of plasma polymerized thin films in microelectronics technology are high dielectric loss and the instability of dielectric parameters when subjected to ambient conditions [35]. High dielectric loss in plasma polymerized films is due to the high concentration of free radicals. To reduce the free radical concentration, thermal annealing of these films was carried out in high vacuum at a pressure of 8×10^{-5} torr for 1 h at 373 K, before the top Al electrode was deposited. Figure 10 clearly shows the effect of post-treatment of plasma polymerized aniline thin films. Dielectric loss is reduced in the post-treated polyaniline thin films. A significant reduction in the dielectric loss can be achieved by changing the polymerization conditions as well as temperature and time of post-treatment.

4. Conclusions

Polyaniline thin films were prepared by ac plasma polymerization technique. Dielectric constant and ac conductivity were determined from the measured values of capacitance and dielectric loss in the frequency range from 100 Hz to 1 MHz and in the temperature range of 300–373 K. Low dielectric constant values were observed for the whole range of frequency scanned. Polyaniline thin films with low dielectric constant are potential candidates to be used as intermetallic dielectrics in microelectronics. FTIR studies reveal that the aromatic ring is retained in the polyaniline, thereby increasing the thermal stability of plasma polymerized aniline thin films. Annealing reduced the dielectric loss of plasma polymerized aniline thin films.

Acknowledgments

M R A thanks the Indian Space Research Organization (ISRO) for financial assistance received under 'RESPOND PROJECT' (File No 10/3/354). S J acknowledges financial support received under a UGC minor research project (UO PLB1/8923/2000). C J M thanks CUSAT for the fellowship.

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