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Low *k* thin films based on rf plasma-polymerized aniline

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Abstract. Thermally stable materials with low dielectric constant ($k < 3.9$) are being hotly pursued. They are essential as interlayer dielectrics/intermetal dielectrics in integrated circuit technology, which reduces parasitic capacitance and decreases the RC time constant. Most of the currently employed materials are based on silicon. Low *k* films based on organic polymers are supposed to be a viable alternative as they are easily processable and can be synthesized with simpler techniques. It is known that the employment of ac/rf plasma polymerization yields good quality organic thin films, which are homogenous, pinhole free and thermally stable. These polymer thin films are potential candidates for fabricating Schottky devices, storage batteries, LEDs, sensors, super capacitors and for EMI shielding. Recently, great efforts have been made in finding alternative methods to prepare low dielectric constant thin films in place of silicon-based materials. Polyaniline thin films were prepared by employing an rf plasma polymerization technique. Capacitance, dielectric loss, dielectric constant and ac conductivity were evaluated in the frequency range 100 Hz–1 MHz. Capacitance and dielectric loss decrease with increase of frequency and increase with increase of temperature. This type of behaviour was found to be in good agreement with an existing model. The ac conductivity was calculated from the observed dielectric constant and is explained based on the Austin–Mott model for hopping conduction. These films exhibit low dielectric constant values, which are stable over a wide range of frequencies and are probable candidates for low *k* applications.

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1. Introduction

The ever-changing scenario in integrated circuit (IC) technology in consonance with Moore's law necessitates that the capacity of RAM chips quadruples every 3 years. Recently, in the ICs, submicron technology has been adapted aided by the employment of excimer lasers. However, this also throws up further challenges, and reduction in size induces cross-talks. One way of tackling this is by introducing appropriate dielectrics which are called interlayer dielectric (ILD)/intermetal dielectrics (IMD) [1]. The performance criteria of such materials are low dielectric constant, thermal stability and processability. Low capacitance obviously reduces the RC time constant and decreases the parasitic capacitance and thus improves the overall speed of ICs. So low k dielectric materials are increasingly becoming important in IC technology, especially for fabricating dynamic random access memories (DRAM). It must be mentioned here that, in IC technology, a low k material has been defined as having a dielectric constant less than that of SiO_2 ($k < 3.9$) [2]. At present, low k materials used in IC technology are based on silicon and they are employed in the form of SiO_2 as ILD/IMD [1, 3, 4]. Hence, the search for alternative low k materials is in progress and the onus of replacing the SiO_2-based ILD/IMD is on polymer-based materials [1, 5]. Some of the potential candidate materials to be used as ILD/IMD are polyimides, polyindan, poly(aryl ether)s, poly(silsesquioxane)s and poly(benzoxazole)s [1].

Plasma polymerization is an inexpensive tool for fabricating organic thin films. This technique results in homogeneous, highly cross-linked and thermally stable polymer thin films. The method of plasma polymerization employs ac/rf/dc and pulsed techniques. Among these, rf plasma polymerization needs special mention since it yields conjugate structures of the polymers, which are supposed to be essential for making conducting thin films. In the past, although much emphasis has been laid in fabricating semiconducting films for devices, not much attention was devoted to plasma-polymerized films for low k applications. In this method, it is possible to vary the physical as well as the chemical properties of these films by altering the process parameters, such as monomer flow rate, pressure in the chamber and RF power. Polymer thin films have wide range of applications in making various devices like LEDs, sensors, super capacitors, rechargeable batteries and as intermetallic dielectrics in ICs [3], [6]–[10]. Optical and semiconducting properties of polyaniline thin films have been the subject of in-depth study

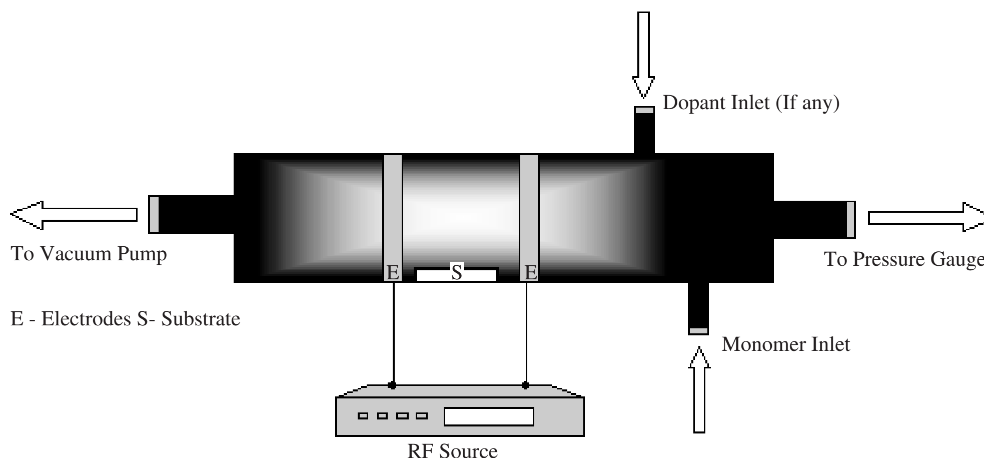

Figure 1. RF plasma-polymerization set-up.

by various researchers [10]. Chemical and electrochemical polymerization of aniline is the usual method for the preparation of bulk polyaniline [11, 12]. RF plasma polymerization is employed for preparing polyaniline thin films. Initial investigations on polyaniline, using ac plasma polymerization technique, indicate that low dielectric materials could be synthesized [5]. This study is a sequel to the ongoing investigations on polyaniline thin films using ac and rf plasma polymerization techniques.

In the present paper, the investigations carried out on the synthesis of rf plasma-polymerized aniline thin films are described. The dielectric permittivity and the ac conductivity are evaluated at different frequencies and temperatures and the results are presented. The results are explained based on a model proposed by Austin and Mott.

2. Experimental techniques

The experimental set-up for the preparation of rf plasma-polymerized aniline is shown in figure 1. It consists of a long glass tube of length 50 cm and of diameter around 8 cm, with provisions for passing monomer vapour, dopants and for evacuation. Chemically and ultrasonically cleaned glass substrates with precoated metal electrodes were placed inside the glass tube exactly under the space separated by the aluminium foil electrodes, which are capacitively coupled and wrapped around the glass tube separated by a distance of 5 cm. The chamber was evacuated and the monomer aniline was passed into the chamber. A glow discharge was obtained in between the electrodes by applying a high frequency (7–13 MHz) and a current in the range 60–80 mA.

Polyaniline thin films were coated under optimum conditions. These coated thin films were shifted to a metal coating unit for coating the counter-electrode. The aluminium electrode was coated by evaporating high-purity aluminium wire under the high vacuum (8×10^{-5} Torr). These films were sandwiched in a cross-sectional area of 2.5×10^{-5} m^2.

The thickness of the film was measured by a homemade set-up employing Tolansky's interferometric method [13]. In this method, the film whose thickness is to be determined, is deposited on an ultrasonically cleaned glass substrate. Above this film, a metal film is evaporated to form a sharp step on the film edge. Another flat glass slide with a semi-transparent film of

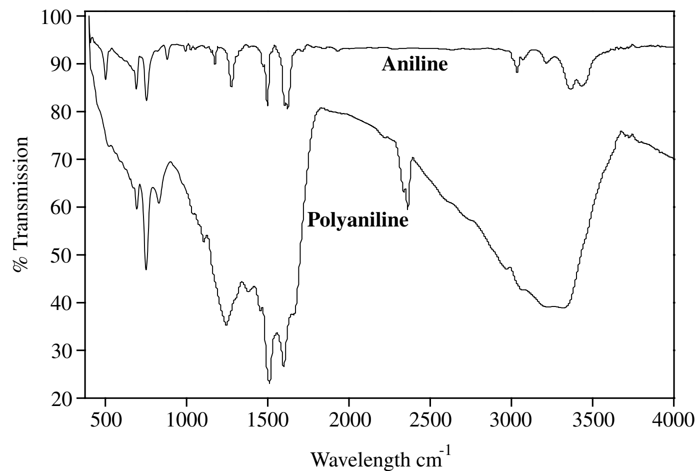

Figure 2. FTIR spectrum of monomer aniline and RF plasma-polymerized aniline.

the same metal is then placed over the specimen with their metal-coated surface in contact with each other so as to leave a small air gap at the step. A monochromatic parallel beam of light passing through the glass plate, inclined at an angle of 45°, is incident on the two-glass plate assembly and reflected light is observed. A set of sharp fringes perpendicular to the step with equal displacements will be observed and the thickness can be determined by using the following relation:

$$t = \frac{D\lambda}{2d}, \tag{1}$$

where D is the displacement of fringes at the step and d the distance between consecutive fringes.

The FTIR spectra of RF polyaniline thin film samples were recorded using a Nicolet Avatar 360 FTIR Spectrophotometer in the wavelength range 400–4000 cm^{-1}, under identical conditions.

Capacitance and dielectric loss were measured using a HP 4192A impedance analyser and a dielectric cell in the frequency range 100 Hz–1 MHz and in the temperature range 300–373 K. The dielectric constant was calculated from the known values of capacitance, thickness and the area of the sample. Furthermore, from the measured values of dielectric constant, dielectric loss and frequency the ac conductivity was calculated using the empirical relation $\sigma_{ac} = 2\pi\varepsilon_0\varepsilon_r \tan\delta$. All these measurements were made under dynamic vacuum.

3. Results and discussions

3.1. FTIR analysis

The FTIR spectrum of monomer aniline and the plasma-polymerized aniline is depicted in figure 2. The peaks in the plasma-polymerized aniline are not sharp when compared with the monomer aniline and most of the IR absorption features of the monomer aniline are noticeable

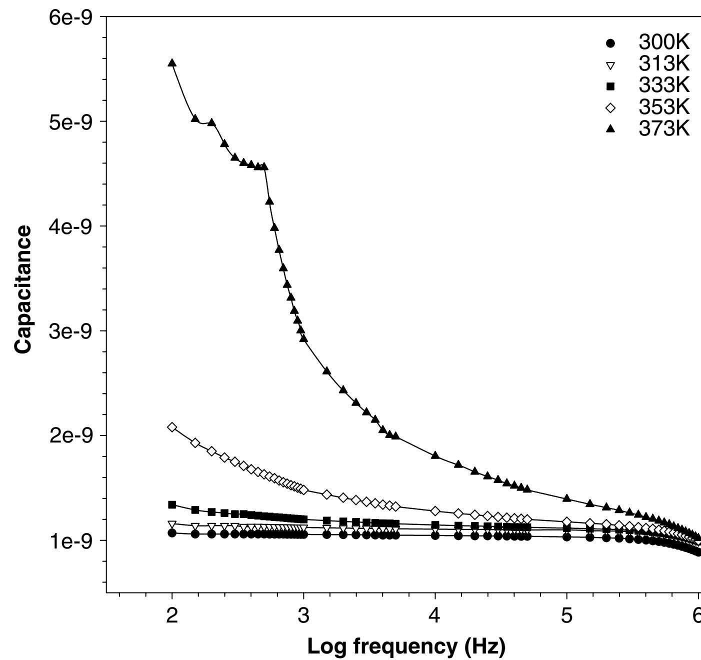

Figure 3. Capacitance of plasma-polymerized aniline thin film as a function of frequency at different temperatures.

in the spectrum of polyaniline with the shift in wave numbers. The peaks at 1511 and 1599 cm^{-1} are indicative of the presence of aromatic ring in the plasma-polymerized aniline [14]. A characteristic peak at 1244 cm^{-1}, which is indicative of the presence of primary aromatic amine (C–N bending), is also found in the spectrum [15]. Two strong peaks at 692 and 751 cm^{-1} indicate the substituted benzene.

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

The capacitance of the plasma-polymerized aniline as a function of frequency at five different temperatures is shown in figure 3. It is evident from the figure that the capacitance is absolutely frequency-dependent. A circuit model proposed by Goswami and Goswami [16] explains this type of behaviour. According to this model, the capacitor system is assumed to comprise a frequency-independent capacitive element C^1 in parallel with a discrete-temperature-resistive element R, both in series with a constant low value resistance r. Based on this model, the measured series capacitance C_s is given by

$$C_s = C^1 + \frac{1}{\omega^2 R^2 C^1} \qquad (2)$$

and the loss is given by

$$\tan\delta = \frac{(1 + r/R)}{\omega R C^1} + \omega r C^1, \qquad (3)$$

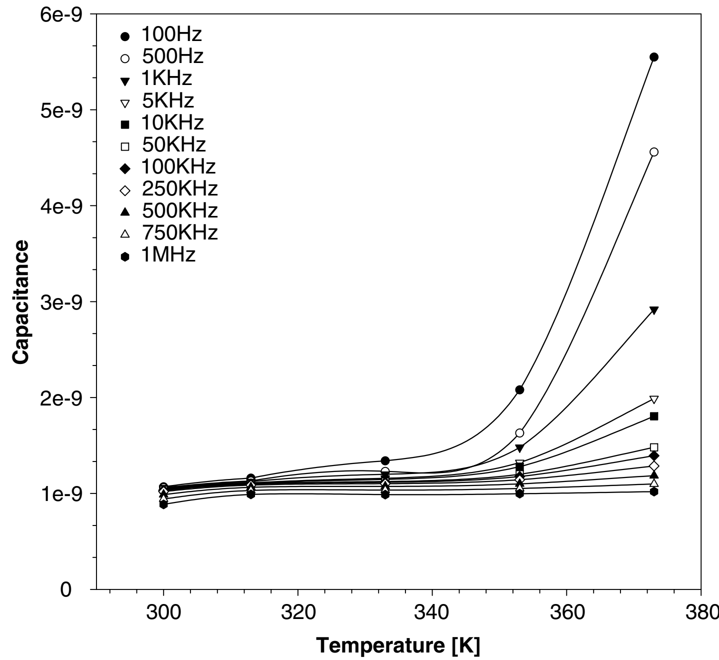

Figure 4. Dependence of capacitance of polyaniline thin film as a function of temperature at different frequencies.

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

$$R = R_0 \exp\left(-\frac{E_a}{KT}\right), \tag{4}$$

where R_0 is a constant and E_a the activation energy. Equation (2) predicts that C_s decreases with increasing ω_s and, at higher frequencies, C_s remains constant for all temperatures. Equation (2) also envisages that, because of the decreasing value of R, C_s will increase with increase in temperature for any frequency. This effect is shown in figures 3 and 4. The variation of loss with frequency at different temperatures is shown in figure 5. From equation (3), it is evident that $\tan\delta$ decreases with increase in frequency till the loss minimum is noted and thereafter $\tan\delta$ increases with increase in frequency. In figure 5, at 373 K, a peak occurs at 350 Hz. It is reported that [17] similar kind of peaks are expected at other temperatures and there occurs a peak shift. This could not be observed in our case since they might be beyond our ac measurement range. This increase in dielectric loss with decreasing frequency is usually associated with ion drift, dipolar polarization or interfacial polarization [17]. The variation of $\tan\delta$ with temperature is shown in figure 6 and is consistent with equation (3). In equation (3), 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 permittivity of plasma-polymerized aniline thin film samples is calculated using the relation

$$C = \frac{\varepsilon_0 k A}{d}, \tag{5}$$

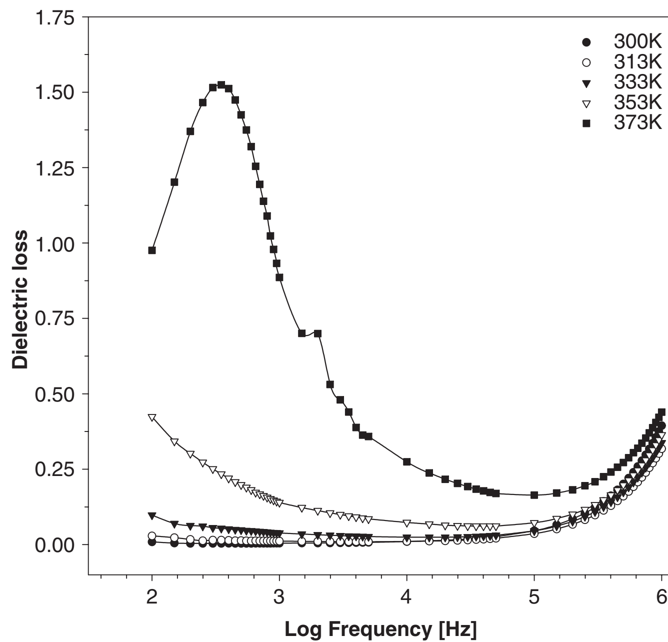

Figure 5. Dielectric loss of polyaniline thin film as a function of frequency at different temperatures.

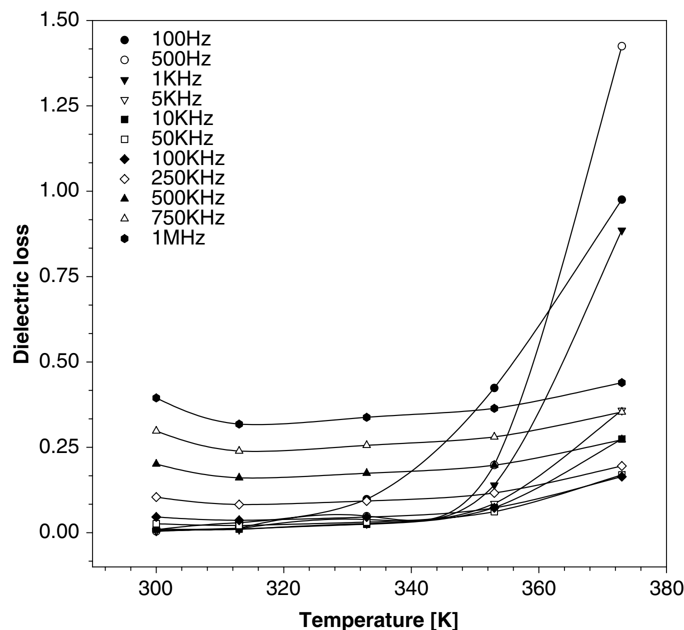

Figure 6. Dielectric loss of polyaniline thin film as a function of temperature at different frequencies.

where C is the capacitance of the sample, A the surface area of the sample ε_0 the permittivity of air and k the dielectric constant of the sample.

The dielectric measurements were carried out in the frequency range 100 Hz–1 MHz. The variations of dielectric constant with frequency at different temperatures were plotted in figure 7.

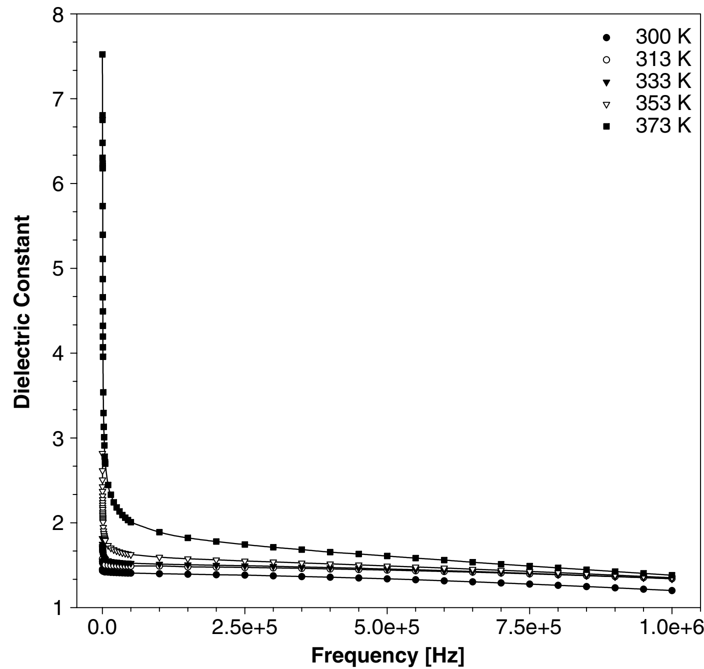

Figure 7. Dielectric constant of polyaniline thin film as a function of frequency at different temperatures.

The dielectric constant lies between 7.52 and 1.38 for the entire frequency range for which the experiment was carried out (300–373 K). The dielectric constant lies between 1.45 and 1.20 at room temperature for the entire frequency, which is considerably low. The characteristics dependence of the dielectric constant can be explained with interfacial polarization. Usually, interfacial polarization is the type of polarization found in the sandwich configuration. Space-charge accumulation at the structural interfaces of an inhomogeneous dielectric material causes interfacial polarization and this was explained by Maxwell and Wagner in terms of a two-layer dielectric model. In microelectronic circuits, RC time delay can be reduced by using this type of low dielectric constant materials as intermetallic dielectrics [1]. The time delay depends on two factors: one is due to the resistance of the interconnections and the other is the capacitance of the dielectric media. RC delay can be calculated by the formula [5]

$$RC = 2\rho k\varepsilon_0 \left[\frac{4L^2}{P^2} + \frac{L^2}{T^2}\right], \tag{6}$$

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 being the metal width and S the space between metals). The dielectric constant of the RF plasma-polymerized aniline thin film is ~1.20. According to equation (6), the dielectric constant of polyaniline with $k = 1.20$ will reduce RC delay by about 70% with respect to SiO_2.

3.4. Ac conductivity as a function of frequency and temperature

The characteristics of ac conductivity (σ_{ac}) as a function of frequency at different temperatures of RF plasma-polymerized aniline thin film is shown in figure 8. It is seen that the conductivity

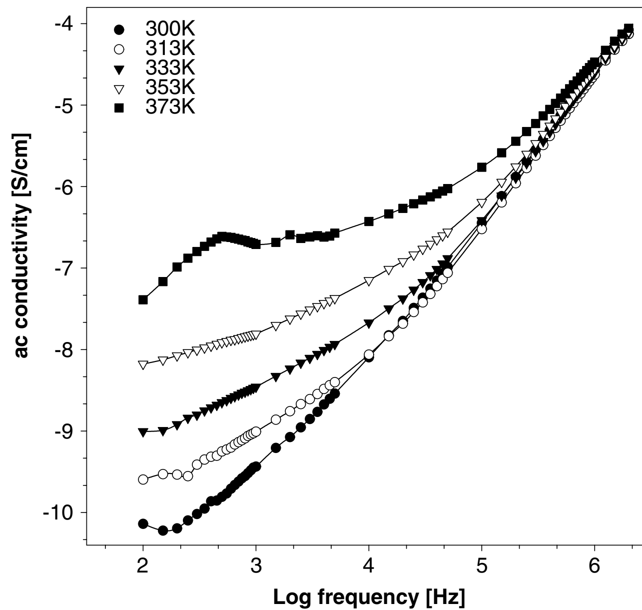

Figure 8. Ac conductivity of polyaniline thin film as a function of frequency at different temperatures.

increases with increase in temperature and frequency. The conductivity increases rapidly at higher frequencies rather than at the lower frequencies.

This can be interpreted by the following empirical relation [18]:

$$\sigma(\omega)\alpha\omega^{n}, \quad (7)$$

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

The values of n were determined from figure 8 and they lie between 0.5 and 1.1 at lower frequencies. The value of n in this frequency range is in accordance with the theory of hopping conduction in amorphous materials [19].

The value of n gives the type of the dominant conduction mechanism in amorphous materials. This power law is an approximation of the Austin and Mott model, which describes the conduction mechanism of ac conductivity. Phonon-assisted hopping of charge carriers through tunnelling from a localized site to another one is the basic physics behind the power-law relation predicted by the Austin and Mott [20]. Mott and Austin also explained the dependence of ac conductivity at lower temperatures by the relation [20]

$$\sigma_{ac} = A\left(\frac{e^{2}}{\alpha^{5}}\right)\{N(E_{F})\}^{2}kT\omega\{\ln\left(\frac{\nu_{ph}}{\omega}\right)\}^{4}. \quad (8)$$

This relation can be written as follows by differentiating with respect to ω

$$\frac{\mathrm{d}\ln\sigma_{ac}(\omega)}{\mathrm{d}\ln\omega} = 1 - \frac{4}{\ln(\nu_{ph}/\omega)}. \quad (9)$$

The value of n also determines the phonon frequency and it depends on the ac frequency [20].

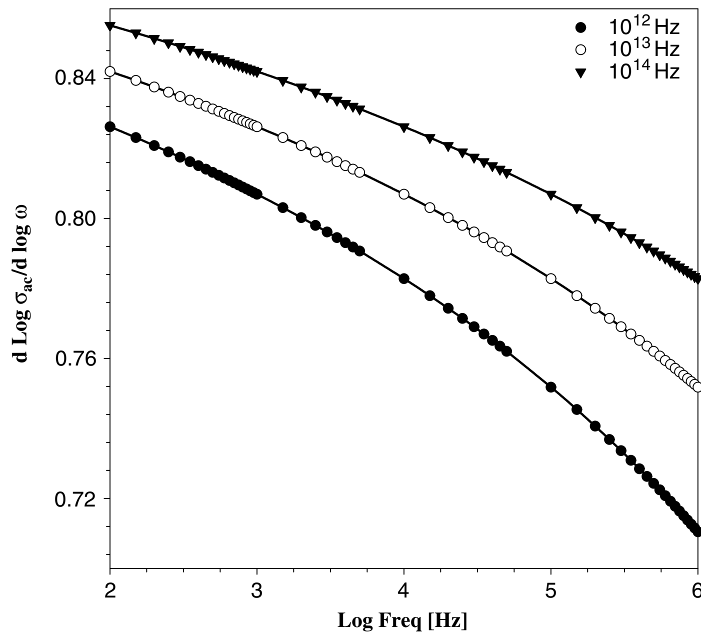

Figure 9. $\mathrm{d}\log\sigma_{ac}/\mathrm{d}\log\omega$ as a function of the frequency for three typical phonon frequencies.

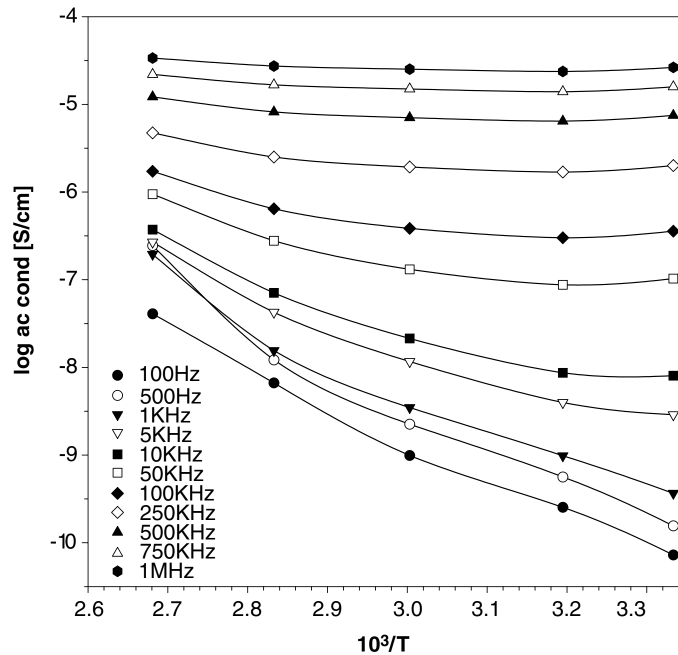

Figure 10. Ac conductivity of polyaniline thin film as a function of temperature at different frequencies.

Figure 9 is the plot of $\mathrm{d}\log\sigma_{ac}/\mathrm{d}\log\omega$ against log frequency for three typical values of $\nu_{ph}(10^{12}, 10^{13}, 10^{14}\,\mathrm{Hz})$. From figure 9 it is seen that, depending on the phonon frequency the value of $\mathrm{d}\log\sigma_{ac}/\mathrm{d}\log\omega$ lies between 0.71 and 0.88 for the entire frequency range. The predicted values of n lie within the values of n obtained from the experiment, provided that a single hopping

ac conductivity mechanism operates in the plasma-polymerized aniline thin films. Based on this it can be concluded that the conductivity is due to hopping. Also it is necessary to compare the experimental and the predicted values for determining whether it is single- or multiple-hopping conductivity [20].

The variation of ac conductivity with temperature as a function of different frequencies is shown in figure 10. Activation energies were calculated and are found to be in the range 0.356–0.1435 eV, which is considerably low. From figure 10 it seems that the ac conductivity of the RF plasma-polymerized polyaniline thin films is frequency-dependent and it has very low activation energy. The low activation energies of these films indicate that a hopping conduction mechanism occurs in RF plasma-polymerized aniline thin films.

4. Conclusion

Polyaniline thin films were prepared using an RF plasma polymerization technique. Dielectric constant and ac conductivity were measured in the frequency range 100 Hz–1 MHz and in the temperature range 300–373 K. The dielectric permittivity in the high-frequency range is considerably low and this type of low dielectric material is a potential candidate as intermetallic dielectrics in microelectronics. Ac conductivity is calculated and the Austin–Mott model is applied to explain the conduction mechanism. FTIR studies reveal that the aromatic ring is retained in the polyaniline, thereby increasing the thermal stability.

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