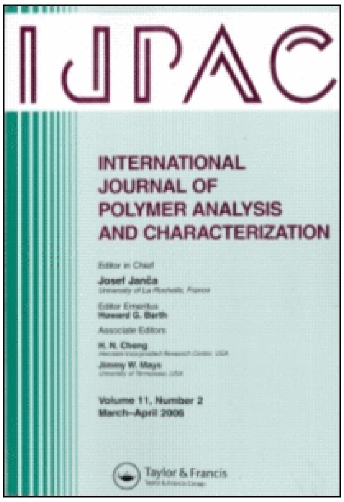

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Microwave Conductivity Measurements of High Conductive Polyaniline Films

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To cite this Article Rmili, Hatem , Miane, Jean-Louis , Olinga, Thomas E. and Zangar, Habib(2004) 'Microwave Conductivity Measurements of High Conductive Polyaniline Films', International Journal of Polymer Analysis and Characterization, 9: 1, 77 — 96

To link to this Article: DOI: 10.1080/10236660490890493

URL: http://dx.doi.org/10.1080/10236660490890493

International Journal of Polymer Anal. Charact., 9: 77–96, 2004
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ISSN: 1023-666X print
DOI: 10.1080/10236660490890493

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Microwave Conductivity Measurements of High Conductive Polyaniline Films

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This article presents several techniques for determining the complex conductivity of highly electrically conducting polymer films at microwave frequencies. The advantages and disadvantages of these techniques are discussed. Microwave measurements were investigated using resonant cavity, reflection/transmission, and impedance surface techniques. The dc conductivity was measured using the four wires technique.

Polyaniline (PANI/DEHEPSA) films of 120 μm thickness have conductivity of (5000–6000 S/m) and permittivity of 6000 ± 1000 over X and S bands. The high values of the measured conductivity and its weak dependence on frequency at least up to 12 GHz confirm the metallic character of Pani films and their efficient use in microelectronic technology such as microwave integrated circuits (MMIC) and microwave devices.

Keywords: Polyaniline films; Microwave; Conductivity; Permittivity

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INTRODUCTION

Conducting polymers have many potential applications in the microelectronics industry since they have been proved to be excellent replacements for metals and semiconductors. Conducting polymers are effective discharge layers[1] as well as conducting resists[2] in electron beam lithography, find applications in metallization of plated through-holes for printed circuit board technology[3], provide excellent electrostatic discharge protection for packages and housings of electronic equipment[4], provide excellent corrosion protection for metals[5], and may have applications in electromagnetic interference shielding[6].

Among a large variety of conducting polymers, polyaniline is preferred for many applications since it offers a number of advantages due to its extensive chemical versatility. Polyaniline (PANI) is generally soluble[7] and relatively stable; it results from the oxidative polymerization of aniline, which is on easy one-step synthesis involving inexpensive raw materials[8]. Also the environmental stability of PANI appears to be good compared to a number of other conducting polymers. For this reason, it is one of the most potentially useful conducting polymers.

The use of polyaniline films in microelectronics, especially microwave printed circuits, requires the study of their electric behavior at high frequencies[9,10]. The two fundamental properties of a conductor at high frequencies are its bulk conductivity and skin depth. Since the quality of conducting films for microwave applications (patch antenna, filters, oscillators, etc.) depends highly on their conductivity and smooth surface, accurate values for microwave conductivity and permittivity are very important for the efficient utilization of these films. In highly conductive polymers, conductivity does not depend on frequency, at least up to 12 GHz.

Microwave techniques for measuring the dielectric properties (permittivity, conductivity, etc.) of insulator and semiconductor materials are well known and have used for a long time[11–13], whereas microwave investigation of high/superconducting materials is still a challenge[14–16].

In this article, measurement procedures are described that allow the determination of microwave properties of high conducting PANI films. We present a number of techniques for microwave characterization of PANI films over S and X bands. These include the resonant method, reflection/transmission method, and impedance surface method. The resonant method extracts the microwave conductivity σ and the penetration depth δ from the measured bandwidth and the resonance frequency of a resonant cavity. The direct reflection/transmission method gives the conductivity σ and the permittivity ε of the film from the reflection/transmission coefficients using a rectangular waveguide. Numeric calculations were performed for the exploitation of the experimental data. The impedance surface method determines both the film's complex conductivity and permittivity from the measured reflection coefficient using an open-ended coaxial probe. On the other hand, the dc conductivity of polyanilne films was investigated by the four wires technique.

PREPARATION OF CONDUCTING FILMS

Polyaniline refers to a class of polymers in which the nonconducting or base form has the general structure shown in Figure 1.

The conducting state of polyaniline can be achieved by the protonation of nitrogen in its 50% oxidized emeraldine state ($y = 0.5$), using protonic acids such as hydrochloric acid (HCl) and camphorsulphonic acid (CSA).

Protonation of polyaniline leads to the formation of polarons and bipolarons along the conjugated chain. The structure of the molecule presents a high charge delocalization, resulting in a half-filled polaron conduction band and an increase in the electrical conductivity, which becomes a function of the dopant concentration.

The mechanism of charge transport in PANI films can be explained by the variable range hopping of charge carriers (polarons, bipolarons, etc.) between randomly distributed localized states[17,18], since conducting polymers are usually classified as highly disordered systems[19].

Polyaniline was synthesized according to the method described in Olinga et al.[20]. The dopant used was 1,2-benzenedicarboxylic acid, 4-sulfo, 1,2di(2-ethyl hexyl) ester (DEHEPSA)[20]. Dichloroacetic acid (DCCA) was used as the solvent in preparing polyaniline solution for film casting. Four grams of PANI/DEHEPSA complex were dissolved in 100 g of dichloroacetic acid (DCCA), and the solution was stirred for 12 h at room temperature. Then 15 mL of final solution (4 wt% of PANI/DEHEPSA) was spread out on a Teflon slide, and the solvent was allowed to evaporate in a vacuum oven for a period of 24 h at 60°C. The obtained films have a thickness of 120 μm.

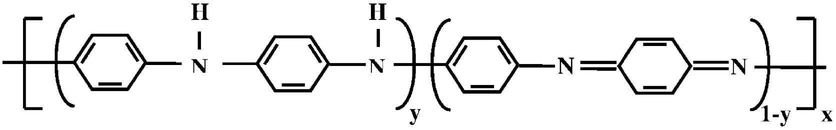

FIGURE 1 Structure of the basic nonconducting form of polyaniline-type polymer Emeraldine base: $y = 0.5$.

EXPERIMENTAL

Resonant Cavity Technique

The determination of conductivity is based on the theory of perturbation[21,22]. The sample is placed in a cavity resonator at the position of maximum magnetic field where the contribution of electric field for the perturbation is minimum. The cavity resonator is of the transmission type. Electromagnetic energy is coupled to the cavity through two coax-to-cavity adapters situated at the top wall of the cavity. A slot is provided in the broad wall of the cavity for the introduction of the sample (see Figures 2–3).

In the case of highly conductive materials, the sample cannot be placed in an electric field, where it will cancel the resonance of the cavity; it is instead placed in a magnetic field, which excites surface currents, providing that the thickness d of the sample is greater than the skin depth δ.

When a microwave magnetic field $\vec{H}$ is applied to the highly conductive PANI film, it appears as a current density $\vec{J}_S$ parallel to the film surface S, producing surface losses:

$$\vec{J}_S = \vec{H} \otimes \vec{n} \tag{1}$$

$\vec{n}$ is the unit vector normal to the film surface.

The mean power loss, caused by Joule effect, is:

$$W_j = \frac{1}{2} \iiint_{V_S} \frac{|\vec{J}|^2}{\sigma} dv \tag{2}$$

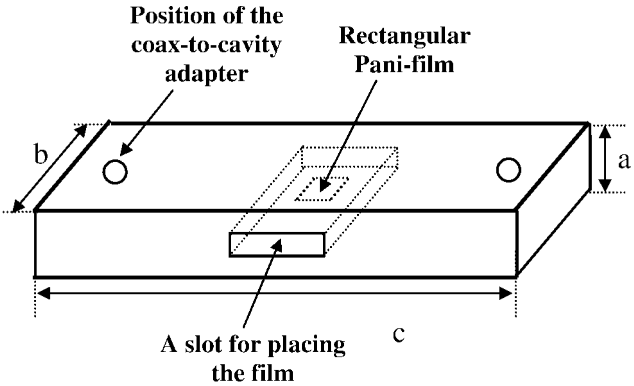

FIGURE 2 Schematic diagram of the resonator cavity containing the sample at the position of maximum magnetic field (center of the cavity).

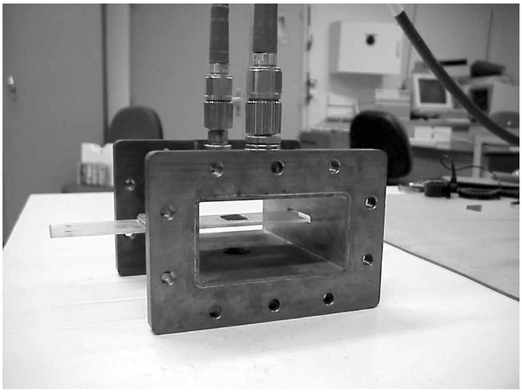

FIGURE 3 View of a resonator cavity; the thin PANI film is put on the sample holder (The two walls of the cavity are removed to show the sample placement).

V_S and σ are respectively the volume and the conductivity of the film, and $\vec{J}$ is the current density given by:

$$\vec{J}(x, y, z) = \vec{J}_S e^{-\frac{1+j}{\delta}z} \tag{3}$$

where z is the direction of propagation and δ is the penetration depth defined as

$$\delta = \sqrt{\frac{2}{\mu_0 \mu_r \omega \sigma}} \tag{4}$$

μ_0 is the magnetic permeability of vacuum, μ_r is the permeability of the film, and ω is the angular frequency.

Substituting Equations (1)–(3) into Equation (4), we get:

$$W_j = \frac{1}{2\sigma\delta} \iint_S |\vec{H}|^2 ds \tag{5}$$

Surface losses due to the high conductivity of the film increase the power dissipated in the cavity, causing a variation of the quality factor,

$$\Delta\left(\frac{1}{Q}\right) = \frac{1}{Q_S} - \frac{1}{Q_0} = \frac{1}{\omega_0} \frac{W_j}{W_T} \tag{6}$$

where Q_0 and Q_S are respectively the quality factor of the empty cavity and the quality factor of the loaded cavity. Quality factor Q is given by $Q = f/\Delta f$, where f is the resonant frequency and Δf is the corresponding 3 dB bandwidth.

W_T is the power of the cavity resonator given by

$$W_T = \frac{\mu_0}{2} \iiint_{V_C} |\vec{H}|^2 dv \tag{7}$$

V_C is the volume of the cavity.
From Equations (5)–(7), we get the expression of the quality factor variation,

$$\Delta\left(\frac{1}{Q}\right) = \left(\frac{\mu_r}{2\mu_0\omega_0\sigma}\right)^{1/2} \frac{\iint_S |\vec{H}|^2 ds}{\iiint_V |\vec{H}|^2 dV} \tag{8}$$

Thus, the film conductivity is expressed as

$$\sigma^{1/2} = \left(\frac{\mu_r}{2\mu_0\omega_0}\right)^{1/2} \frac{1}{\Delta(\frac{1}{Q})} \frac{\iint_S |\vec{H}|^2 ds}{\iiint_V |\vec{H}|^2 dv} \tag{9}$$

For the dominant TE_{012} mode in a rectangular waveguide, the components of the magnetic field (Figure 4) within the cavity can be expressed as

$$H_x = 0 \tag{10}$$

$$H_y = j\frac{2H_0b^2}{ac} \sin\left(\frac{\pi}{b}y\right) \cos\left(\frac{2\pi}{c}z\right) \tag{11}$$

$$H_z = H_0 \cos\left(\frac{\pi}{b}y\right) \sin\left(\frac{2\pi}{c}z\right) \tag{12}$$

where a is the height, b the width, and c the length of the waveguide cavity resonator. H_0 is the amplitude of the magnetic field.

The small width ($\lambda < 10\,\mathrm{mm}$) of the conducting sample allows neglecting the perturbation of the electric field in the cavity by the presence of the sample. For a small rectangular film placed in the center of

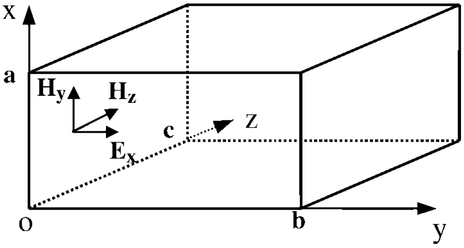

FIGURE 4 Configuration of TE_{012} mode.

the cavity, we can suppose that the magnetic field is uniform at the proximity of the film surface.

Therefore, we have $H_x = H_y = 0$ and

$$H_z = -j\sqrt{\frac{\varepsilon_0}{\mu_0}}\frac{2b}{\sqrt{4b^2 + c^2}}E_0 \tag{13}$$

At high frequencies the current is concentrated near the top and the bottom of the conducting film; the total surface interacting with the electromagnetic field then becomes 2 S (S is the surface of the film).

Then we get

$$\iint_S |\vec{H}|^2 ds = 2E_0^2\frac{\varepsilon_0}{\mu_0}\frac{4b^2}{4b^2 + c^2}S \tag{14}$$

The stored power in the cavity, W_T, can be evaluated as

$$\iiint_V |\vec{H}|^2 dv = \frac{\varepsilon_0}{\mu_0}E_0^2\frac{abc}{4} \tag{15}$$

Finally, from Equations (9), (14) and (15), we get the film conductivity:

$$\sigma^{1/2} = 16\left(\frac{2}{\mu_0\omega}\right)^{1/2}\frac{b^2}{(4b^2 + c^2)abc}\frac{S}{\Delta(\frac{1}{Q})} \tag{16}$$

The experimental setup consists of a HP 8510B vector network analyzer, a sweep oscillator, an S-parameter test set, and a rectangular cavity resonator. The design parameters of the cavity are shown in Table I.

Samples prepared in the form of a thin rectangular film are put on a sample holder, introduced into the cavity through the slot, and placed at the center of the cavity, where the magnetic field is maximum and parallel to the film.

The resonant frequency and quality factor of the cavity resonator were measured. All measurements were done in S band (3.94 GHz) at 25°C.

TABLE I Design parameters of the cavity

Dimensions of the cavity (mm)	S band
Height, a	86
Width, b	43
Length, c	125

Transmission Line Technique

Theory

A transmission line method was used in order to determine the microwave conductivity of a highly conductive PANI film that fills the cross section of a rectangular waveguide. This method consists in measuring the modulus of both the reflection and transmission coefficients S_{11} and S_{21} and in extracting the complex conductivity and permittivity. The conducting film is placed in the waveguide for reflection/transmisransmission measurements (see Figures 5–6). It was assumed that only the fundamental mode TE_{10} of the electromagnetic field was propagating through the waveguide.

The reflection coefficient S_{11} of the structure, defined as the ratio of the reflected to the incident electric field E_r/E_i, is given by

$$S_{11} = \frac{r(1 - e^{-2\gamma d})}{1 - r^2 e^{-2\gamma d}} \tag{17}$$

where r is the reflection coefficient from the air conductor interface and γ the propagation constant in the sample.

The transmission coefficient S_{21} through the film is defined as the ratio of the transmitted to the incident electric field E_t/E_i. Including multiple reflections in the film, the transmission coefficient can be presented as

$$S_{21} = \frac{(1 - r^2)e^{-\gamma d}}{1 - r^2 e^{-2\gamma d}} \tag{18}$$

The term $e^{-\gamma d}$ represents the propagation through the film. Taking into account the metallic character of the film, the penetration depth δ of the electromagnetic field in the material is smaller than the film thickness d

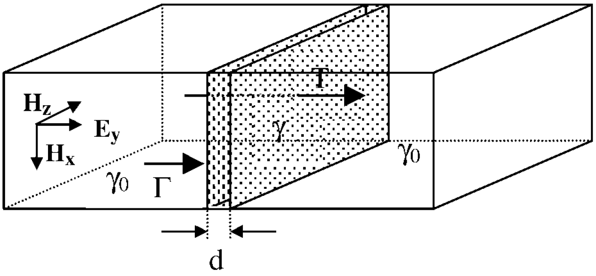

FIGURE 5 Description of thin PANI film placement in rectangular waveguide.

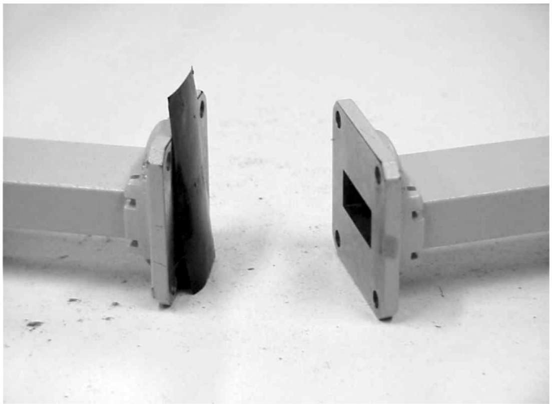

FIGURE 6 View of the sample position in the rectangular waveguide.

and we can suppose that $e^{-\gamma d} \ll 1$. Then Equations (17) and (18) can be simplified to

$$S_{11} \approx r \tag{19}$$

$$S_{21} \approx (1 - r^2)e^{-\gamma d} \tag{20}$$

The reflection coefficient r from the air conductor interface is equal to

$$r = \frac{\gamma_0 - \gamma}{\gamma_0 + \gamma} \tag{21}$$

where γ_0 is the propagation constant in the air and γ is the propagation constant in the conducting film.

According to the standard notation

$$\gamma = \alpha + j\beta \tag{22}$$

where α is the attenuation constant and β the phase constant.

In the air-filled rectangular waveguide, the propagation constant γ_0 is equal to

$$\gamma_0 = j\frac{2\pi}{\lambda_0}\sqrt{1 - \left(\frac{\lambda_0}{\lambda c}\right)^2} \tag{23}$$

whereas the propagation constant γ in the film is related to the material's complex permittivity:

$$\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon' - j\frac{\sigma}{\varepsilon_0 \omega} \tag{24}$$

and γ is given by the equation

$$\gamma = j\frac{2\pi}{\lambda_g} = j\frac{2\pi}{\lambda_0}\sqrt{\varepsilon' - j\frac{\sigma}{\varepsilon_0 \omega} - \left(\frac{\lambda_0}{\lambda c}\right)^2} \tag{25}$$

where λ_g is the wavelength in the waveguide loaded with sample, λ_0 the wavelength in the air-filled waveguide, and λ_c the cutoff wavelength of the TE_{10} mode in the material-filled waveguide.

Measurement Setup and Procedure

The waveguide sample holder is inserted in the measuring device. The test ports of an HP 8510 vector network analyzer is connected via two coax-to-waveguide adapters to the two sections of the waveguide. The sample is placed between the two sections of waveguide. S_{11} and S_{21} parameters were measured by the network analyzer. The measurement procedure consists of following stages:

1. The HP network analyzer is calibrated in the X-band frequency range 8–12 GHz by using a calibration kit that carries out the full two-port calibration method provided by HP Corporation.
2. By using a short circuit as a termination instead of the film placed in the waveguide, the reflection coefficient $(S_{11})_{cc}$ is measured. Next, the reflection coefficient $(S_{11})_{mes}$ of the film is measured and the rapport $(S_{11})_{cc}/(S_{11})_{mes}$ is calculated. Thanks to this operation, the calibration plane situated at the coax/waveguide adapter interface is transported to the measurement plane (air/film interface) to which the measured reflection coefficient must be referred. This operation provides the suppression of the undesirable reflection at the coax/waveguide adapter interface.

From Equations (19) and (20), we can get the modulus of S_{11} and S_{21},

$$|S_{11}| \approx |r| \tag{26}$$

$$|S_{21}| \approx \left|1 - r^2\right| e^{-\alpha d} \tag{27}$$

The HP network analyzer directly measures modulus of S_{11} and S_{21} coefficients as

$$\left|S_{11}^{dB}\right| = 20\log|r| \tag{28}$$

$$\left|S_{21}^{dB}\right| = 20\log\left|(1-r^2)e^{-\alpha d}\right| \tag{29}$$

and we get ε and σ by numerical inversion of these relations.

Surface Impedance Technique

Theory

The microwave conductivity of highly conductive PANI films can be determined by measuring the surface impedance. The method consists of measuring the reflection coefficient S_{11} at the coax/film interface in order to determine the surface impedance Z_S and deduce the film conductivity σ using the equivalent circuit parameters of the probe[23,24].

The microwave surface impedance is used to describe the electromagnetic response of the conducting materials. It is defined by the ratio of the surface electric field to the surface current density and is expressed as[25]

$$Z_S = (1-j)\sqrt{\frac{\pi\mu_0 F}{\sigma}} \tag{30}$$

When a plane wave is normally incident on a layer of conducting PANI film of thickness d, the wave is partially reflected and partially transmitted. The reflected wave at the front interface is characterized by the reflection coefficient S_{11}, which depends on the dielectric properties of the material, namely, the conductivity and the permittivity.

The reflection coefficient S_{11} at the coax/polyaniline film interface is given by:

$$S_{11} = |S_{11}|e^{j\varphi} = \frac{Z_S - Z_0}{Z_S + Z_0} \tag{31}$$

where Z_0 is the characteristic impedance of the coax ($Z_0 = 50\ \Omega$).

Then, from Equations (30) and (31) we get the expression of the microwave conductivity:

$$\sigma = \pi\mu_0 F\left[\frac{(1-j)\left(1-|S_{11}|e^{j\varphi}\right)}{Z_0(1+|S_{11}|e^{j\varphi})}\right]^2 \tag{32}$$

where the complex conductivity, $\sigma(\omega) = \sigma'(\omega) + j\sigma''(\omega)$, and the complex permittivity, $\varepsilon(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$, of the material are related by the following equations:

$$\varepsilon'(\omega) = \frac{\sigma''(\omega)}{\varepsilon_0 \omega} \tag{33}$$

$$\varepsilon''(\omega) = \frac{\sigma'(\omega)}{\varepsilon_0 \omega} \tag{34}$$

where ε' and ε'' are the real and imaginary parts of the complex permittivity, respectively, and σ' and σ'' are the real and imaginary parts of the complex conductivity, respectively.

Equations (32)–(34) show that the conductivity and the permittivity of PANI films can be determined by measurement of the modulus $|S_{11}|$ and the argument φ of the complex reflection coefficient.

Measurement Procedure

An open-ended coaxial-line probe was connected to an HP 8510B vector network analyzer for dielectric measurements. The test film is placed at the end of a coaxial line having an outer radius b, an inner radius a, and the characteristic impedance Z_0. Table II gives the design parameters of the probe. The geometry of the open ended coaxial probe is shown in Figure 7.

The sample used is backed by a short-circuit termination and fixed with a movable sample holder to ensure that the probe maintains complete and stable contact with the sample to avoid errors caused by air gaps. We assume that the thickness d of the film is greater than penetration depth δ to avoid the influence of multiple reflections inside the film. The material to be tested is assumed to extend to infinity in the radial direction.

The modulus $|S_{11}|$ and the argument φ of S_{11} were measured by means of the vector network analyzer calibrated over the frequency range 8–12 GHz in the reflection mode with a response type calibration. The measurements were performed at the selected frequency $F = 10\,\text{GHz}$.

TABLE II Design parameters of the open-ended coaxial line probe

Parameters of the probe	X band
Dielectric: Teflon	$\varepsilon_r = 2$
Inner radius, a (mm)	0.255
Outer radius, b (mm)	0.838

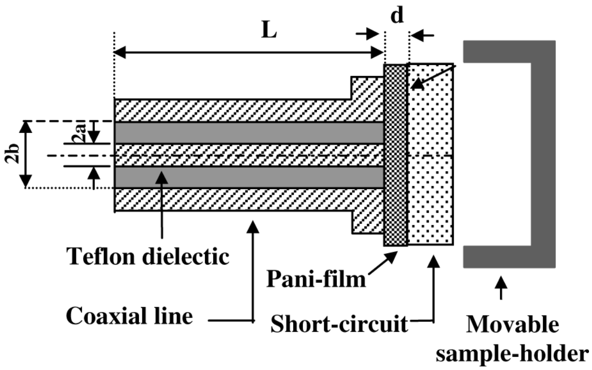

FIGURE 7 Sample configuration for measuring the conductivity using an open-ended coaxial line.

RESULTS

Four Wires Technique (dc)

The four wires technique[26] was used to investigate the dc conductivity of PANI films. Figure 8 displays the U-I characteristic from which the dc conductivity is extracted.

At room temperature, application of currents in the range 0.1–50 mA shows an ohmic behavior. From Figure 8, it can be seen that the measurements and the curve fit follow closely each other. The curve fit through the average measured voltages has a regression factor of $R = 0.993$, where $R = 1$ indicates a perfect fit. Measurements performed on four PANI films of depth 120 μm give a mean dc conductivity of 6000 ± 300 S/m.

Resonant Cavity Technique (F = 3.94 GHz)

The last two columns of Table III show the conductivity and penetration depth values of PANI films measured at 3.94 GHz, with the resonant cavity technique. In order to ensure the repeatability of the measurement procedure, four samples with different dimensions were tested. The means values of the conductivity and skin depth are respectively 5560 ± 350 S/m and 107 ± 3 μm.

Transmission-Line Measurements (F = 10 GHz)

By using the transmission-line technique, S_{11} and S_{21}coefficients were measured over X band and tabulated in Table IV. S_{11} and S_{21} coefficients

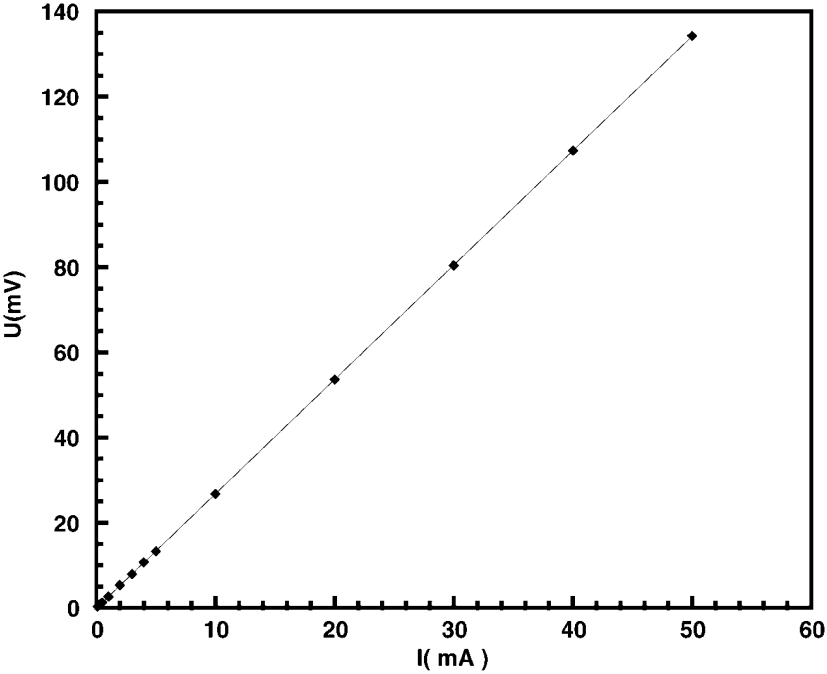

FIGURE 8 U-I characteristic of a PANI film determined by the four wires technique.

have slight variations with frequency over the frequency range 8–12 GHz. Therefore, numeric calculations were performed at the selected frequency F = 10 GHz in order to determine the conductivity and the permittivity of PANI films. First, discreet values of ε and σ were selected in the range 1000–10,000. For each couple (ε, σ) the values $20\log|S_{11}|$ and $20\log|S_{21}||$ were calculated according to Equations (17)–(29). Figure 9 presents the chart $(S_{11}, S_{21}) = f(\varepsilon, \sigma)$.

TABLE III Conductivity and penetration depth of PANI films at 3.94 GHz

PANI film	Length, L (mm)	Width, λ (mm)	Surface, S (mm^2)	Conductivity, σ (S/m)	Penetration depth, δ (μm)
Sample 1	20	10	200	5995	103
Sample 2	10	9	90	5623	108
Sample 3	15	5	75	5287	110
Sample 4	13	9	117	5333	110

TABLE IV Measured values of S_{11} and S_{21} modulus over X band

F (GHz)	S_{11}(dB)	S_{21}(dB)
8	−0.158	−30.4
9	−0.166	−30.2
10	−0.170	−30.0
11	−0.175	−29.9
12	−0.181	−29.7

Calculated values of S_{11} and S_{21} for several values of σ and ε are shown in Figure 9. The positioning of the measured values of S_{11} and S_{21}in the chart allows the determination of the conductivity σ and estimate the permittivity ε.

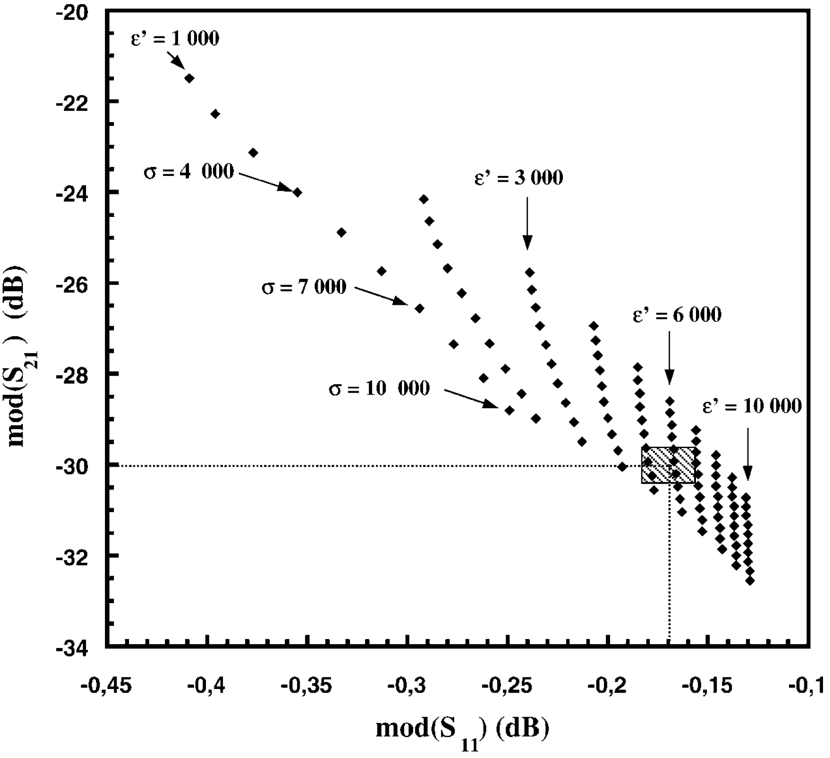

FIGURE 9 Chart $(S_{11},S_{21}) = f(\varepsilon,\sigma)$ determined by numeric calculations at F = 10 GHz.

Measurements at 10 GHz show that for a sample thickness of 120 μm the mean value of the reflection coefficient $S_{11}$was −0.17 dB with a standard deviation of ±0.02 dB and the mean value of the transmission coefficient S_{21} was –30 dB with a standard deviation of ±0.5 dB. According to Equations (17)–(29), the accuracy of the conductivity and permittivity measurements depends on the accuracy with which modulus of S_{11} and S_{21} can be measured. As a result, at 10 GHz, PANI film has a conductivity of 6000 ± 600 S/m and has a permittivity of 6000 ± 500.

On average, the conductivity of PANI films can be determined using this reflection/transmission technique, with ±10% error. Repeatability of the measurements was checked by measuring modulus of S_{11} and S_{21} of three PANI samples five times each.

Surface Impedance Technique (F = 10 GHz)

By means of the surface impedance technique, the complex microwave conductivity and permittivity of PANI films were investigated. The modulus and the argument of the reflection coefficient S_{11} were measured. It is found that at the frequency F = 10 GHz, $|S_{11}|$ is -1.01 ± 0.02 dB and φ is $177 \pm 0.5°$.

The real parts of both the complex conductivity and permittivity were determined theoretically according to Equations (30)–(34).

Figures 10–11 display the dependence of the conductivity and the permittivity of PANI films on both the modulus and phase of S_{11}. They show that σ and ε increase as S_{11} modulus is increased, especially for high modulus values. It can be seen that the effect of the phase errors on the conductivity and the permittivity is significant, especially for high reflection values that characterize high conducting films.

At 10 GHz, PANI film of thickness 120 μm has a conductivity of 6000 ± 500 S/m and a permittivity of 7360 ± 1000.

DISCUSSION

Table V shows the conductivity and permittivity values of PANI films determined by four techniques.

The resonant method technique offers the highest accuracy in the measurement of microwave conductivity but only the real part of the complex conductivity is accurately determined at only one frequency. The small measurement uncertainties are due to errors of the location of the sample in the cavity.

One important advantage of the microwave reflection/transmission technique is to determine simultaneously both the complex conductivity and permittivity, although precision measurement can be performed for only a narrow range of material thickness. Measurement errors are

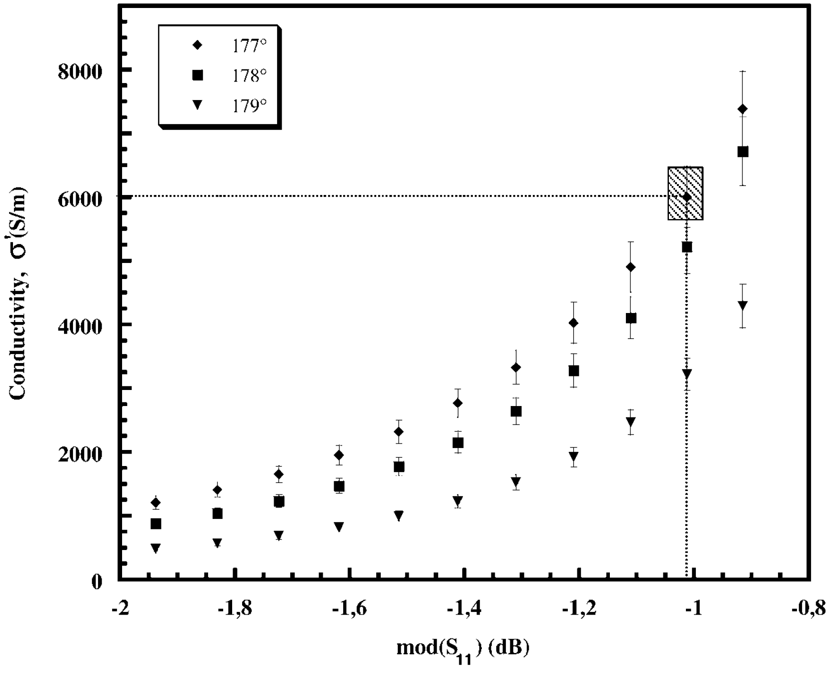

FIGURE 10 The real part of the complex conductivity versus S_{11} modulus for three phase values.

thought to be related to calibration errors and multiple reflections inside the film.

The attractiveness of the open-end coaxial probe measurement technique coupled with the impedance surface method has arisen from the broadband measurement capabilities, the simplicity of sample preparation, and the relative ease of the measurement procedure, but the measurement results depend highly on the pressure exerted by the probe on the film. The waveguide technique and the resonance cavity do not suffer from this inconvenience. Using this technique, we can determine both the complex conductivity and permittivity. Therefore, for high conducting films, the accuracy of the results depends highly on the phase errors. These errors are caused by air gaps between the sample and the probe and the exerted force on the film by the sample holder.

The choice of measurement approach is mostly determined by the shape, consistency, and extension of the film to be characterized. For example, measurements on thick ($d \gg \delta$) and rigid films can be advantageously performed by the open-coaxial method. Small samples of well-defined shapes can be measured at a single frequency by the resonant

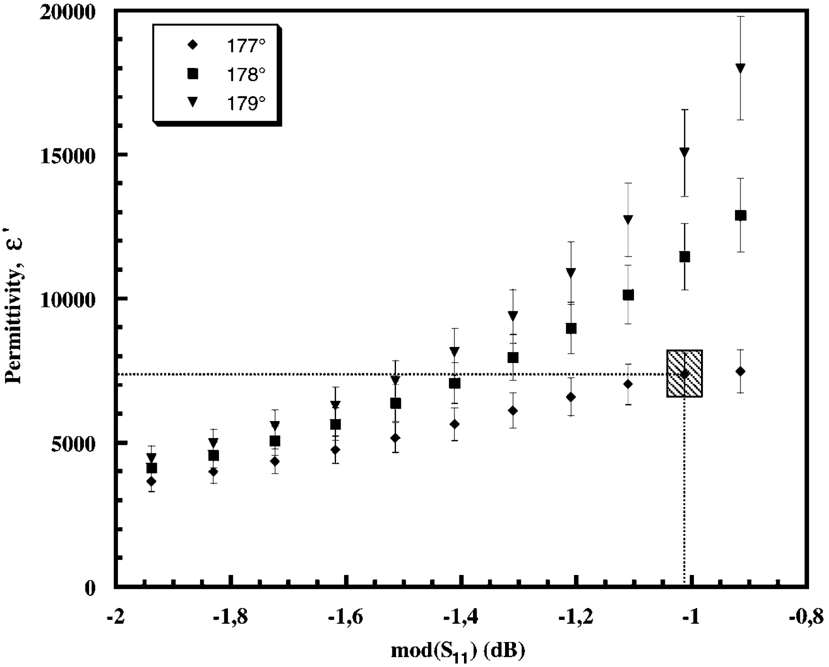

FIGURE 11 The real part of the complex permittivity versus S_{11} modulus for three phase values.

cavity technique. Large sheet and/or thin films ($d \gg \delta$) can be characterized by the reflection/transmission technique.

CONCLUSION

In this article, we have presented a number of microwave techniques for convenient, fast, and relatively accurate measurements of high

TABLE V Conductivity values of PANI films measured with different methods

Measurement technique	Conductivity, $\sigma \pm \Delta\sigma$ (S/m)	Permittivity, $\varepsilon' \pm \Delta\varepsilon'$
Four wires, dc	6000 ± 5%	—
Resonant cavity, F = 3.94 GHz	5560 ± 6%	—
Transmission line, F = 10 GHz	6000 ± 10%	6000 ± 8%
Impedance surface, F = 10 GHz	6000 ± 8%	7360 ± 10%

conducting PANI films at high frequencies. In order to prove their efficient use in microelectronic technology, PANI films were charaterized over S and X bands by resonant cavity, reflection/transmission, and coaxial probe techniques. The advantages and disadvantages of these techniques were discussed. Experimental measurements of the conductivity and the permittivity were performed on films of 120 μm thickness and different dimensions at room temperature. The dc conductivity was investigated by the four wires technique.

The experimental data indicate that at high frequencies, it's difficult to determine accurately the conductivity and the permittivity of high conducting PANI films, due to the small penetration depth ($\delta < 65\,\mu\text{m}$) of electromagnetic fields ($\vec{E}$ and $\vec{H}$) in the film and the high dependence of the measured quantities on measurement errors, which differ from one technique to other.

However, further improvement is needed in the measurement process to remove small errors related to calibration error, air gaps between the film and the probe, line losses, connector mismatch, and location of film in the test structure.

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