# APPLICATIONS OF THERMOELECTROMETRY TO METAL-ION MODIFIED POLYIMIDE FILMS

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As part of a research program to decrease the electrical resistivity of polyimide films with ionic additives a variable temperature three probe electrical resistivity measurement system has been designed and constructed. Sample temperature, electrification time, atmosphere, and measurement mode are computer controlled. As a data interpretation aid, temperature cycled analysis can be routinely performed. Surface resistivities in the range $10^3$–$10^{15}$ ohm and volume resistivities in the range $10^5$–$10^{18}$ ohm-cm are theoretically measurable under well controlled experimental conditions from room temperature to 250°. The electrical resistivity measurement system is useful for the evaluation of polymer films or films in general. Application of the system for analysis of cobalt, lithium and tin ion-modified polyimide films and some experimental considerations are presented. Correlation of the electrical measurements with differential scanning calorimetry, thermomechanical analysis, and thermogravimetric analysis is demonstrated.

Thermoelectrometry, thermogravimetry (TG), and differential scanning calorimetry (DSC) are useful methods of thermal analysis. However, compared with TG and DSC thermoelectrometry techniques are not often used. A recent review by Wendlandt [1] indicated that thermoelectrometry accounted for 2.2% of all the techniques used in Thermochimica Acta and 1.4% of the techniques used in Journal of Thermal Analysis. Because thermoelectrometry boasts sensitivity several orders of magnitude greater than DSC for the detection of the glass transition [2] and may yield data of a more fundamental nature than other thermal methods, large growth in the area of thermoelectrometry is expected.

There are two key reasons why thermoelectrometry, the measurement of resistance, conductance, capacitance or other electrical property as a function of time and temperature in controlled environment, is a valuable technique for the materials scientist. First, it allows direct evaluation of a fundamental material property (i.e. resistivity) at variable temperatures. This information is quite useful in microelectronic applications where it is important to evaluate the electrical resistivity as a function of temperature of polymers which are used as passive layers

and encapsulants. Such knowledge is critical since for a constant current an increase in Joule heating of the electronic device may occur. As the "feature-size" of components decreases giving rise to a greater number of elements per unit area, temperature dependent resistivity data should become even more valuable. Secondly, although the exact nature of the conduction process may not be of primary importance to the materials scientist, resistivity versus temperature plots may yield detailed information regarding polymer dynamics. Since charge carrier mobility may be inversely proportional to the microviscosity of the polymeric medium, an abrupt change in resistivity in the temperature region of a polymer transition can be anticipated.

The purpose of this paper is to discuss some experimental considerations that are applicable to the evaluation of the electrical resistivity of polymer films. Application of the measurement system to polyimide films which have been lightly doped with soluble metal salts have been evaluated in this regard. The complementary nature of electrical resistivity measurement to the more commonly employed thermal methods of analysis will also be presented.

## Measurement equipment

Our research group has been studying the effect of metal salt and metal complex incorporation into polyimide films [3–6]. The resulting films would be employed in the construction of large structures for use in outer space. A primary goal of the research is to decrease the electrical resistivity of polyimide films while maintaining the high mechanical integrity and the high thermal stability characteristic of nonmodified polyimide [7, 8]. A computer controlled, three probe, variable temperature electrical resistivity measurement system (VTERM) developed in our laboratory allows evaluation of these ion-modified polymer films or films in general. The system which has been previously discussed [9] is shown schematically in Figure 1. The instrumentation measures both surface and volume (bulk) electrical resistivity. This is an important feature because while many insulators have low bulk conductivity (reciprocal of resistivity) they may have appreciable surface conductivity [10]. The well defined geometry of the circular electrodes having dimensions as shown in Figure 2 allows calculation of electrical resistivity from the measured electrical current, applied voltage and sample thickness. Further, the electrode dimensions are the same as those of a Keithley 6105 Resistivity Adapter which is commercially available, allowing direct comparison of room temperature measurements with the variable temperature measurements. If the electrode geometry is not known and does not remain constant during the experiment only empirical resistance, not resistivity, can be determined. The
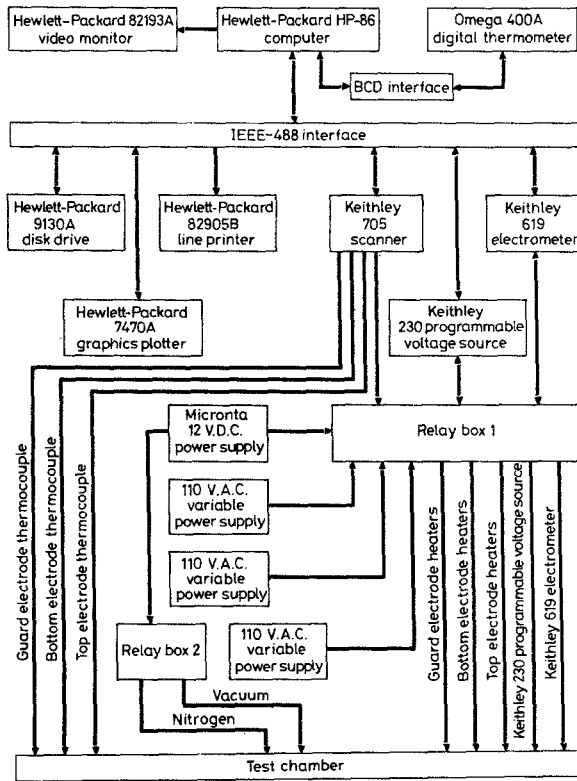
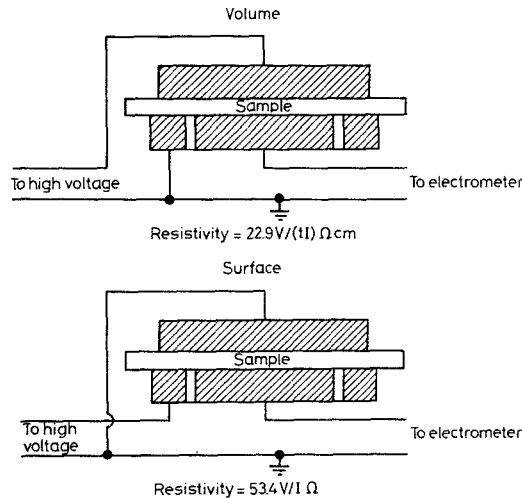Fig. 1 Components of the three probe variable temperature electrical resistivity measurement system (VTERM)



Fig. 2 Electrode geometry for surface of volume resistivity measurements. Top electrode 76 mm diameter, bottom electrode 50.8 mm diameter, and guard electrode 57.2 mm inside diameter. $V$ = voltage, $I$ = current, $t$ = film thickness

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VTERM system controls sample temperature, electrification time, atmosphere, and measurement mode in addition to automatically storing, printing, and plotting the data with the associated computer peripherals. A schematic of the electrical resistivity test cell is shown in Figure 3.
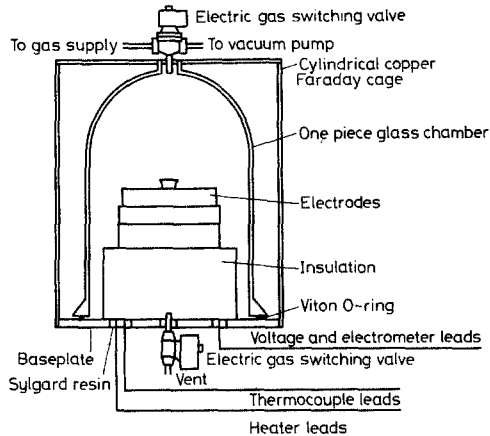


**Fig. 3** Schematic of the variable temperature controlled atmosphere test cell for electrical resistivity measurements

Crucial to the successful evaluation of the electrical properties of highly resistive materials is the measurement system itself. In this regard, because currents as low as $10^{-14}$ ampere may be field induced, careful electrical isolation of the test cell is necessary. The importance of this concern is illustrated by the analysis of a commercially available DuPont Kapton polyimide film (25.4 μm thick). Kapton was chosen as a sample partly because its resistivity, though not unique among insulators [8], is the highest the equipment is expected to encounter. Few polymers have electrical resistivity as high as Kapton does and the intention of our research work is to reduce the electrical resistivity of polymers. Also, vendor supplied volume resistivity versus temperature data were available. Figure 4a shows the analysis of the sample with a carefully constructed test cell which exhibits substantial leakage current (minimum measured current $\approx 10^{-10}$ amp). The leakage current is responsible for the lack of information (i.e. essentially zero slope) from 20° to 125°. Some workers, when the electrical resistivity at 25° is greater than $10^{16}$ ohm-cm and cannot be obtained directly (similar to Figure 4a), extrapolate the high temperature region of the resistivity versus temperature plot to obtain the value of the parameter, $\varrho$ 25°C [11]. Extrapolation of our resistivity versus temperature data in Figure 4a yields $\varrho$ 25°C equal to $5 \times 10^{17}$ ohm-cm. After more consideration was given to proper grounding, guarding, and shielding [12], the results shown in Figure 4b were obtained. Because of the reduced leakage current
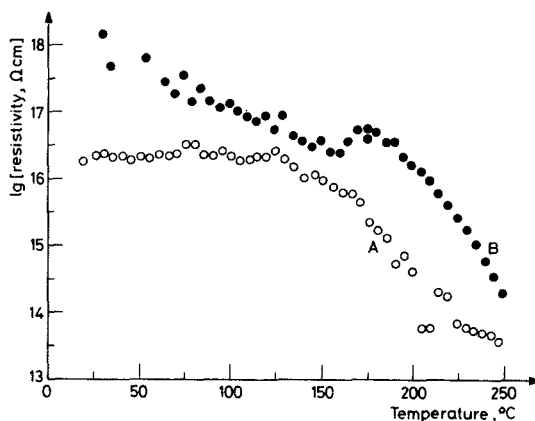
**Fig. 4** Volume resistivity of DuPont Kapton film with a) substantial leakage current; b) reduced leakage current

(minimum measured current $10^{-14}$ amp) electrical properties were directly obtained at and above room temperature ($\varrho$ 25°C obtained directly from Figure 4b = $1.05 \times 10^{18}$ ohm-cm). Vendor literature indicates the volume resistivity is $1 \times 10^{18}$ ohm-cm. Thus, good agreement between our electrical resistivity data (3 significant figures) and data reported by DuPont for Kapton polyimide (1 significant figure) is evident and substantiates that the measurements are valid.

**Electrification time**

An important consideration in the evaluation of the resistivity of highly insulative materials is the polarization or electrification time [10]. The proper electrification time can be obtained from a plot of current versus time or charge versus time as shown in Figure 5. At short times polarization currents dominate the measurement and would result in falsely low direct current electrical resistivity values for the sample. At longer times the influence of polarization current is diminished and the d.c. conductivity current is obtained. From the plot it is found that the d.c. electrical resistivity of a cobalt modified polyimide film [13] can be obtained at times greater than about 2 minutes. Highly accurate results may require longer times as there is still a slight slope to the $i$–$t$ plot. The charge versus time plot becomes linear as the influence of polarization current is reduced. In our variable temperature electrical resistivity measurements the sample is poled with 100 volts and is left poled throughout the duration of the experiment to minimize the influence of electrode charging current and polarization current.
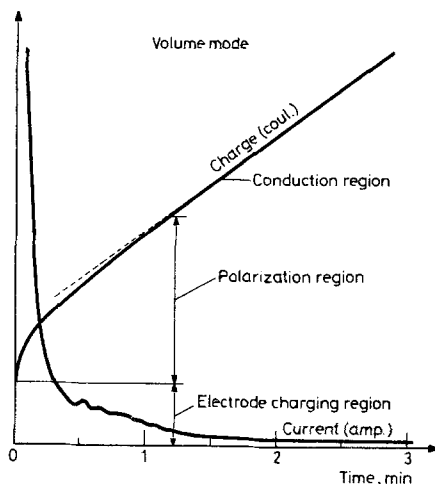
**Fig. 5** Current versus time and charge versus time for a cobalt modified BDSDA/ODA polyimide film. BDSDA is 4,4′-bis(3,4-dicarboxyphenoxy)diphenylsulfide and ODA is oxydianiline

## Measurement atmosphere

It is well known that sample atmosphere strongly affects the electrical response of a material to temperature variation, especially those materials having high electrical resistivity. The influence of measurement atmosphere on the d.c. electrical resistivity of a polyimide film modified with lithium chloride [3] is shown in Figure 6. Volume resistivity versus temperature profiles were obtained on identical films both conditioned in air prior to analysis but one was analyzed in *air* and the other
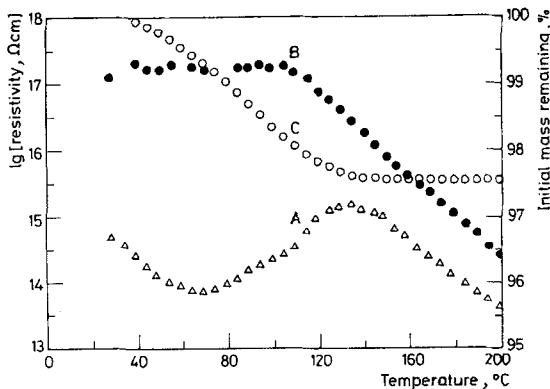


**Fig. 6** Volume resistivity of a lithium modified polyimide film analyzed in a) air and b) vacuum, and c) the thermogravimetric curve

was analyzed in *vacuum*. Electrical resistivity values were considerably lower at temperatures up to 120° for the film analyzed in air (Figure 6a) compared with the film analyzed in vacuum (Figure 6b). The measured electrical resistivity during the cooling cycle was the same for the film analyzed in vacuum and the film analyzed in air and both were comparable to the first heating cycle in vacuum. Reanalyzing either film in air (after re-conditioning the film in air prior to analysis) results in a resistivity versus temperature profile similar to the first heating cycle (Figure 6a) and similar to the first cooling cycle and subsequent heating-cooling cycles (Figure 6b) indicating that the polyimide properties can be reversibly changed by sorbed species. The difference in the data between 25° and 120° suggests that sorbed water has a significant influence on the electrical resistivity. Decreased electrical resistivity of polyimide films (and polymers in general) containing moisture may be attributed to three primary reasons: the inherent ability of moisture to provide charge carriers, the ability of moisture to increase the effective dielectric constant of the polymeric medium thereby increasing the extent of dissociation of ionizable groups [14], and the ability of water to act as a plasticizer. Fourier transform infrared spectrometry has been previously used to verify substantial water sorption by the lithium-doped polyimide film [3]. Figure 6 shows a correlation between the electrical resistivity of the film analyzed in air (Figure 6a) and the mass loss of the same film independently determined by thermogravimetry (Figure 6c). Mass loss occurs in the same temperature region as where the electrical resistivity (measured with air atmosphere) undergoes the greatest change with increasing temperature (i.e. resistivity decreases with increasing temperature up to about 60°, increases between 60° and $\sim$120°, and finally decreases again at temperatures above 120° similar to the film analyzed in vacuum).

## Complementary data

As previously mentioned the mobility of charge carriers may be inversely proportional to the microviscosity of the polymeric medium. As charge carrier mobility increases the resistivity will decrease as defined by the fundamental equation

$$\frac{1}{\varrho} = \sum_i n_i e_i \mu_i$$

where  $\varrho$ = resistivity, ohm · cm
  $n_i$ = concentration of $i$-th charge carrier, cm$^{-3}$
  $e_i$ = charge on $i$-th charge carrier, coulombs
  $\mu_i$ = charge mobility of $i$-th charge carrier, cm$^2$ V$^{-1}$s$^{-1}$
  $i$ = carrier species

The glass-transition is a temperature region in which volume, heat capacity, and polymer chain mobility increase. Dilatometry, differential scanning calorimetry, and dynamic mechanical analysis can each be used to characterize the polymer (bulk) glass transition temperature region. Electrical resistivity measurements, even though the charge carrier mobilities and the number of charge carriers can not be separated, reveals the glass transition because the greatly enhanced mobility of charge carriers arising in this regime leads to an abrupt decrease in electrical resistivity. Figure 7 shows the complementary nature of DSC and the VTERM analysis for a cobalt modified polyimide film. The DSC scan, second heating cycle, is shown in Figure 7a. An abrupt change in heat capacity, having a midpoint at
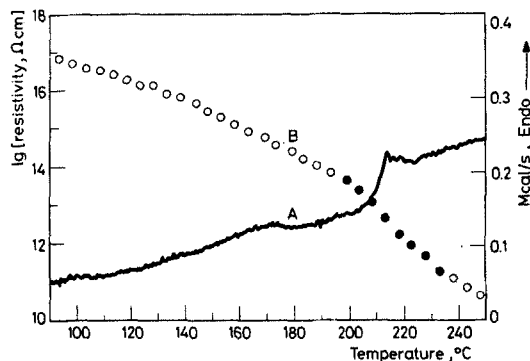


Fig. 7 Differential scanning calorimetric analysis (A) and variable temperature volume electrical resistivity (B) of a cobalt modified polyimide film

208°, indicates a glass-transition. Figure 7b is an analysis of another sample of the same film using the VTERM system. A change in the slope of the log resistivity versus temperature curve is observed at 203°. Thermomechanical analysis indicated a polymer transition at 213°. The coincidence of these three independent observations indicates that the electrical resistivity (VTERM) is responding to the same material change as that evidenced by both the heat capacity (DSC) and volume (TMA) change (i.e. increased conserted chain segment mobility of the polymer matrix).

## Surface versus volume resistivity

Many of the modified polyimide films developed in our laboratory have surface properties extremely different from volume properties, in contrast to nonmodified polyimide films. An example, shown in Figure 8, compares the surface resistivity with the volume resistivity of a tin modified film [6]. Auger electron/argon ion

etching profiles indicated a tin species concentrated within the first 1000–1500 Å on the surface of the modified film [6]. X-ray photoelectron spectroscopy has indicated binding energies for the tin species consistent with tin(IV) oxide [6]. The resistivity of bulk $SnO_2$, depending on the type and amount of impurity, is $10^8$ ohm or less [15]. The surface electrical resistivity data for the tin-doped polyimide are consistent with the semiconductor behaviour (i.e. $10^6 - 10^7$ ohms) expected for tin(IV) oxide (Figure 8b). The volume electrical resistivity data, on the other hand, suggest that polymer bulk electrical properties have not been significantly altered by incorporation of the tin complex (Figure 8a). This too is consistent with the Auger electron spectroscopy depth profile data in that only a small amount of tin is found in the bulk of the film. Thus the film is highly anisotropic, having moderately low surface resistivity but extremely high bulk resistivity.
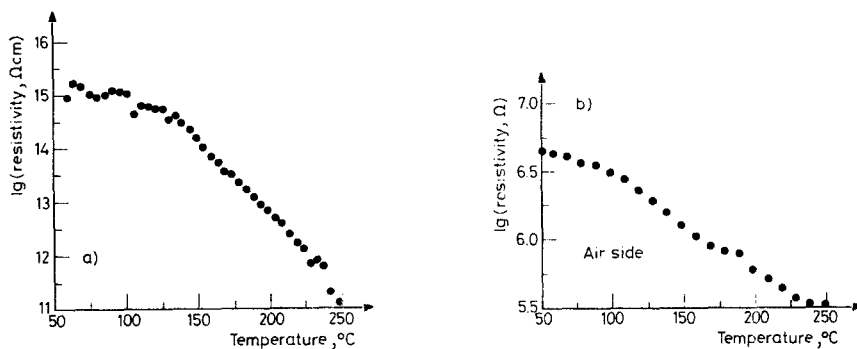


**Fig. 8** Volume electrical resistivity (A) and surface electrical resistivity (B) as a function of temperature for a tin modified BTDA/ODA polyimide film. BTDA is 3,3', 4,4'-benzophenonetetracarboxylic dianhydride and ODA is oxydianiline

## Conclusions

It has been shown that extreme care must be taken to reduce leakage currents when designing a system to measure surface and volume electrical resistivity of highly insulative materials. Sample chamber atmosphere control is important because the sample atmosphere, especially moisture, can have a severe influence on the electrical properties of polymeric films. The data arising therefrom can be valuable to the materials scientist in that the influence of environment and thermal history on electrical properties can be probed. Furthermore, similar to all thermal methods of analysis, a variable temperature controlled atmosphere measurement system allows direct evaluation of materials under conditions similar to their anticipated end-use. The ability to measure surface resistivity or volume resistivity

is valuable for materials having surface contamination or intentional charge dissipation additives or materials having anisotropic electrical characteristics. Electrical properties can also be used, independent of the source of charge carriers, to probe polymer dynamics. The ability of detect bulk polymer transitions was demonstrated. This allows for confident implementation of thermoelectrometry as a problem solving and material evaluation tool.

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**Zusammenfassung** — Als Teil eines Forschungsprogramms zur Herabsetzung des elektrischen Widerstandes von Polyimidfilmen mit ionischen Additiven wurde ein 3-Proben-Meßsystem zur Ermittlung des elektrischen Widerstandes in Abhängigkeit von der Temperatur entworfen und konstruiert. Probentemperatur, Elektrisierungszeit, Atmosphäre und Meßmethoden waren computergesteuert. Als Dateninterpretationshilfe kann eine hinsichtlich der Temperatur zyklische Analyse routinemäßig ausgeführt werden. Die Oberflächenwiderstände sind im Bereich von $10^3$–$10^{15}$ Ohm und die Volumenwiderstände im Bereich von $10^5$–$10^{18}$ Ohm-cm unter gut kontrollierten experimentellen Bedingungen von Raumtemperatur bis 250° theoretisch meßbar. Das elektrische Widerstandmeßsystem ist nützlich für die Bewertung von Polymerfilmen oder Filmen im allgemeinen. Die Anwendung des

Systems zur Analyse von mit Co-, Li- und Sn-Ionen modifizierten Polyimidfilmen und einige experimentelle Hinweise werden angegeben. Es wird gezeigt, daß die mit dem beschriebenen System erhaltenen Resultate mit durch DSC, thermomechanische Analyse und TG erhaltenen Werten korrelieren.

**Резюме** — С целью исследования уменьшения электрического удельного сопротивления полиимидных пленок, модифицированных ионными добавками, разработана и изготовлена аппаратура для измерения электрического удельного сопротивления в зависимости от температуры проб. ЭВМ контролировала температуру пробы, время электризации, атмосферу и тип измерения. С помощью программ проведена вспомогательная интерпретация данных и анализ цикла температур. При тщательно контролируемых экспериментальных условиях поверхностное электрическое удельное сопротивление может быть теоретически измерено в интервале $10^3$–$10^{15}$ ом, а объемное электрическое удельное сопротивление в области $10^5$–$10^{18}$ ом при температурах от комнатной до 250°. Система для измерения электрического удельного сопротивления является полезной для оценки как пленок в целом, так и полимерных в частности. Показано использование такой системы для анализа полиимидных пленок, модифицированных ионами кобальта, лития и олова, а также представлены некоторые экспериментальные соображения. Представлена корреляция электрических измерений с данными дифференциальной сканирующей калориметрии, термомеханического и термогравиметрического анализов.