polymer papers

A.c. electrical behaviour of cobalt-complex-doped polyimide films

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A series of solvent-compatible cobalt-complex-doped polyimide films have been evaluated for their a.c. electrical behaviour. The doped films display different dielectric character compared to their undoped counterpart, the extent being dependent on the dopant concentration. Temperature studies show a hysteresis effect, which is attributed to moisture pick-up by surface cobalt on the film.

(Keywords: a.c. characteristics; polyimides; metal-doped polymers; dielectrics)

INTRODUCTION

The study of metal doping into polyimides has formed one field of research activity in recent years. The initial impetus, that of obtaining good electrical conductivity in polyimides, has given rise to the study of other characteristics. The development of polyimide films with a semiconductive metal oxide surface derived from cobalt, lithium and tin compounds is one such example[1,2]. Significantly missing, however, are studies on the influence of metal doping on the a.c. characteristics of polyimide films. The a.c. behaviour of metals in polyimides could be of some interest in the semiconductor field. This is because one common application of polyimides is as insulators in semiconductor devices. Low levels of metal loading could be looked at from the viewpoint of trace impurities. It is desirable to evaluate their influence on the dielectric characteristics of the polymer. Recently there have been some reports on the effect of metal halides on the electrical properties of polyimides, which have included dielectric behaviour[3,4]. We have also embarked on our own programme of evaluating the a.c. character of these materials. In light of this, we wish to present our results on a.c. behaviour measurements of a series of cobalt-doped polyimide films.

EXPERIMENTAL

The synthesis and standard characterization of cobalt-doped polyimide films are reported elsewhere[5].

Thin polyimide film samples were coated with thin layers of polymer-based silver paint on both sides of the sample, to serve as electrodes. The a.c. electrical behaviour was evaluated using the three-terminal method and employing a Hewlett Packard 4192A LF Impedance Analyzer. The frequency was varied between 100 Hz and 10 MHz. The temperature ramp (from ambient to ~100°C) was imposed by placing the set-up in a glass container, which was subsequently immersed in a water bath. Temperature was detected using a type T thermocouple.

RESULTS AND DISCUSSION

A.c. electrical behaviour has been measured for cobalt-doped polyimide films derived from two solvent-compatible cobalt complexes, $CoCl_2 \cdot MDA$ (4,4′-methylenedianiline) and $CoCl_2 \cdot PDA$ (1,4-phenylenediamine), developed in our laboratories with a monomer combination of 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) and oxydianiline (ODA). Four films for each dopant, containing different levels of doping as summarized in *Table 1*, were chosen for this study in order to evaluate the influence of percentage metal in the polyimide films.

Of particular interest are the responses of dielectric constant (ε) and dissipation factor ($\tan \delta$) to varying frequency and the effect of temperature on the two properties.

Response of ε to frequency

Figures 1 and *2* show plots of ε vs. frequency for the two series. The plot of the reference undoped BTDA-ODA derived polyimide shows typical constant behaviour over most of the frequency range, with a tailing increase at high frequencies similar to the trend reported in ref. 3 for PMDA-ODA derived polyimide. The plots of the doped films display a dopant concentration effect. In each group of samples, it was found that, if the cobalt concentration is below 1.5%, the ε values of doped

Table 1 Summary of cobalt-doped polyimide films

Dopant[a]	Dopant/polymer ratio	Amount of cobalt in film (%) Found	Calc.
$CoCl_2 \cdot MDA$	2:1	3.66	4.19
	4:1	2.18	2.37
	8:1	1.26	1.28
	16:1	0.75	0.66
$CoCl_2 \cdot PDA$	2:1	3.41	4.19
	4:1	1.93	2.46
	8:1	1.30	1.28
	16:1	0.66	0.67

[a] MDA, 4,4′-methylenedianiline; PDA, 1,4-phenylenediamine

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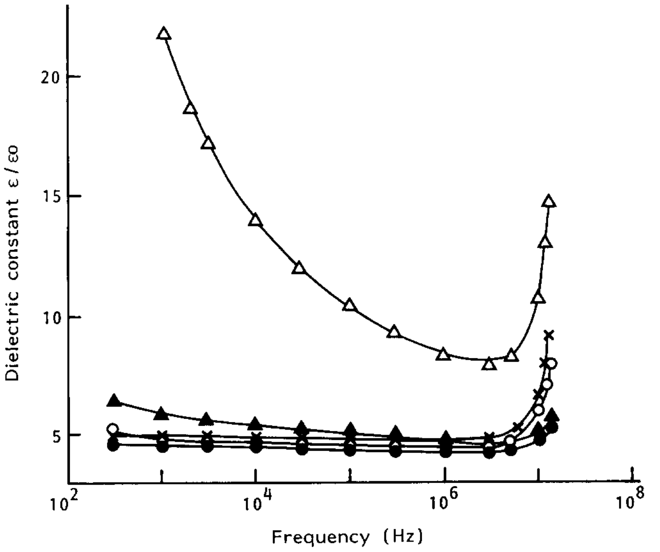

Figure 1 Logarithmic plots of $\varepsilon/\varepsilon_0$ vs. frequency for $CoCl_2 \cdot$MDA doped polyimide films. Percentage of Co: (×) 0, (●) 0.75, (○) 1.26, (▲) 2.18, (△) 3.66

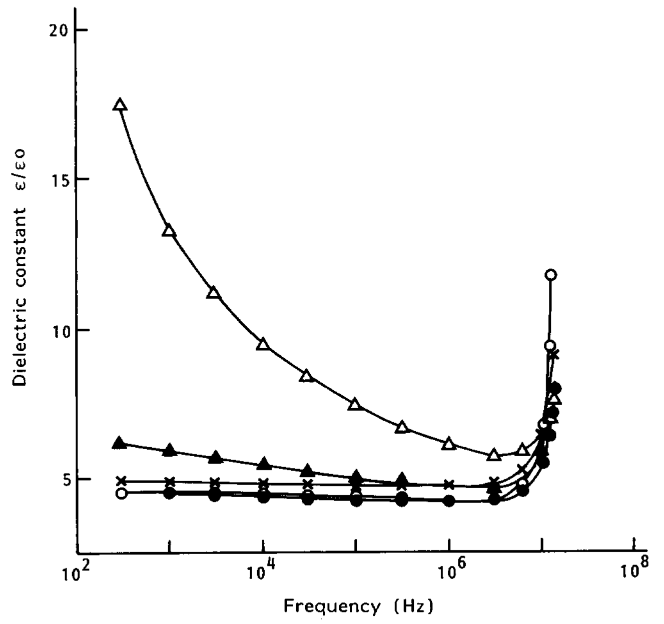

Figure 2 Logarithmic plots of $\varepsilon/\varepsilon_0$ vs. frequency for $CoCl_2 \cdot$PDA doped polyimide films. Percentage of Co: (×) 0, (●) 0.66, (○) 1.30, (▲) 1.93, (△) 3.41

samples are less than that of the undoped sample over almost the entire range of frequency measured. However, when the cobalt concentration is greater than 1.5%, ε exceeds that of the undoped sample. In the case of the two highly doped samples (3.66% and 3.41%), ε is very much larger than in the undoped sample. While the behaviour of ε for the weakly doped cobalt samples is qualitatively in agreement with that reported in ref. 3, the very much enhanced ε at high cobalt concentration is more in line with the observations reported in ref. 4. This is not unexpected because the doping level reported in ref. 3 was 1% and that in ref. 4 was 10% by weight of the prepolymer. There appears to be no influence on ε due to the character of the two dopant types. This is not surprising because the differences in the dopant affects only solubility in the prepolymer stage and the dopant is essentially cobalt ions in the cured film.

The marked differences in dielectric-constant behaviour among the doped films is interesting because it suggests that very low levels of doping (which can be considered as contamination) are not detrimental to the performance of polyimides if they are used as insulators. There appears to be a threshold level beyond which ε increases exponentially across the entire frequency range. This drastic change in ε can be attributed first of all to moisture uptake by the film (see below), secondly to increased interfacial polarization and lastly to ionic conductivity, as a result of high cobalt ion levels in the film. This is not unreasonable because previous work[6] has shown that the dopant usually forms a thin semiconductor layer on the surface of the polymer film, giving rise to heterogeneous layers. This would result in high interfacial polarization in doped films, thus increasing ε. Furthermore, the dopant essentially behaves like cobalt ions, which can become mobile under the influence of an external field. This is typically a low-frequency effect, and the plots of the two highly doped samples support this explanation.

The onset of the formation of the thin cobalt layer may also contribute to the rapid increase of ε, above a threshold cobalt concentration, in another manner. The dielectric constant ε is dependent on the thickness of the film sample. At low cobalt concentrations, there is no formation of a thin cobalt oxide layer, and hence influences on ε are essentially those stated above. On the other hand, as the percentage of cobalt in the film increases, the formation of a cobalt oxide layer sets in. This effectively decreases the film thickness, which is translated graphically into an increase in ε.

Response of tan δ to frequency

Figures 3 and *4* display the response of tan δ to the variation in frequency. All doped samples show higher tan δ than the undoped film below 2 MHz. In particular, for the samples with the two highest cobalt concentrations tan δ is many times larger than for the undoped sample in

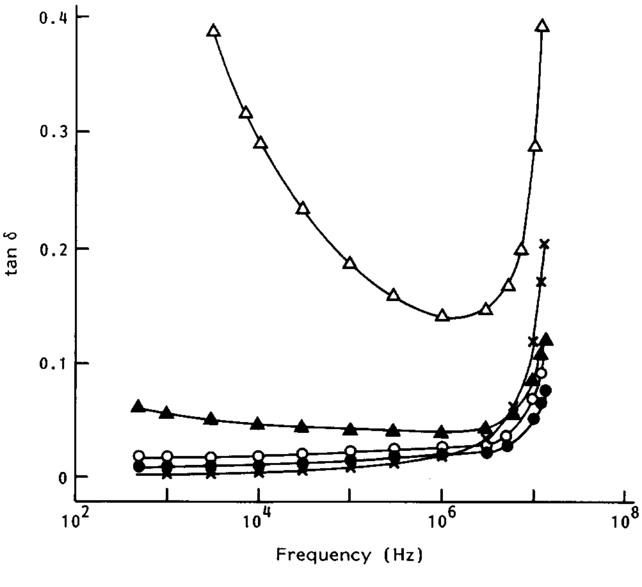

Figure 3 Logarithmic plots of tan δ vs. frequency for $CoCl_2 \cdot$MDA doped polyimide films. Percentage of Co: (×) 0, (●) 0.75, (○) 1.26, (▲) 2.18, (△) 3.66

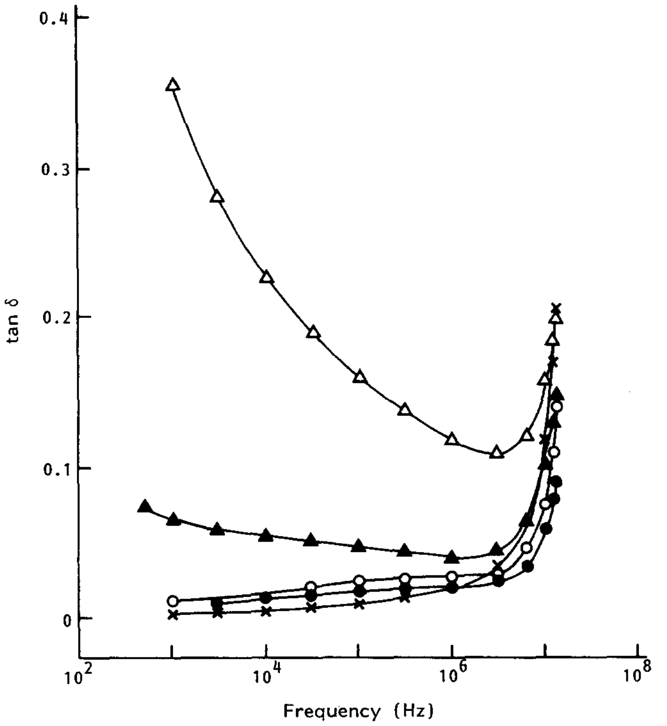

Figure 4 Logarithmic plots of tan δ vs. frequency for $CoCl_2$·PDA doped polyimide films. Percentage of Co: (×) 0, (●) 0.66, (○) 1.30, (▲) 1.93, (△) 3.41

the lower-frequency domain. Above this frequency, however, a reversal is observed, i.e. tan δ of the undoped sample increases rapidly.

The data suggest that, in the low-frequency region, the character of the dopant predominates. The higher lossy character could be attributed to ion mobility derived from the cobalt ions present in the film. An added feature could be that the doped systems behave like a composite, with regions of metal and polymer. This would increase the dissipation factor by giving rise to predominantly interfacial polarization, an effect that would be absent in the undoped sample. This is not unreasonable because this effect is usually enhanced by the presence of moisture (see below).

On crossing to the higher-frequency region, these effects become less important because dipole polarization effects predominate. The backbone of the polymer is made up of alternating regions of carbonyl and imide groups, sites that contribute to dipole polarization. The relatively higher concentrations of these functional groups in the undoped polymer when compared to the doped samples obviously mean that the response of tan δ in the undoped polymer should be higher. Furthermore, local neutralizing interactions by such functional groups with cobalt ions could occur.

Response of tan δ to temperature

Two samples were selected for evaluating the effect of temperature on tan δ. *Figure 5* shows how tan δ reacts to increasing temperature from ambient at various frequencies at a doping level of 3.66% cobalt. The response is found to be more pronounced at low frequencies and the values of tan δ are widespread, covering a range of 0.03 to 0.45 at 1 kHz. The large decrease in tan δ in the low-temperature region has previously been attributed to the terminal –COOH and $-NH_2$ groups[3] in the polymer. We believe, however, that a more likely explanation is the pick-up of moisture by surface cobalt[6]. This can be elucidated if one complete heat–cool cycle is evaluated.

Figure 6 shows the variation of tan δ to temperature at 10 MHz for the 2.18% and 3.66% doped $CoCl_2$·MDA polyimide films (10 MHz was chosen to exclude contributions from ionic conductivity). Apparently, the values of tan δ for these doped films undergo a hysteresis on warming followed by cooling. The entire heat–cool cycle lasted about 7 h, with a waiting time of about 30 min between successive temperature measurements.

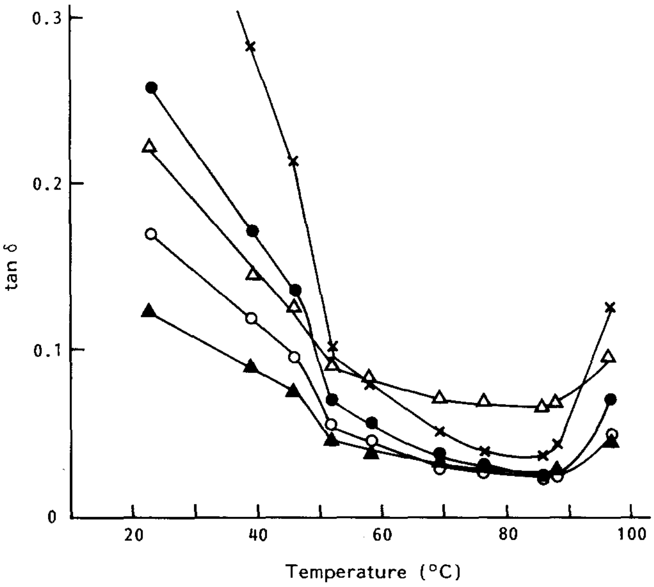

Figure 5 Semilogarithmic plots of tan δ vs. temperature for 3.66% $CoCl_2$·MDA doped polyimide films: (×) 1 kHz, (●) 10 kHz, (○) 100 kHz, (▲) 1 MHz, (△) 10 MHz

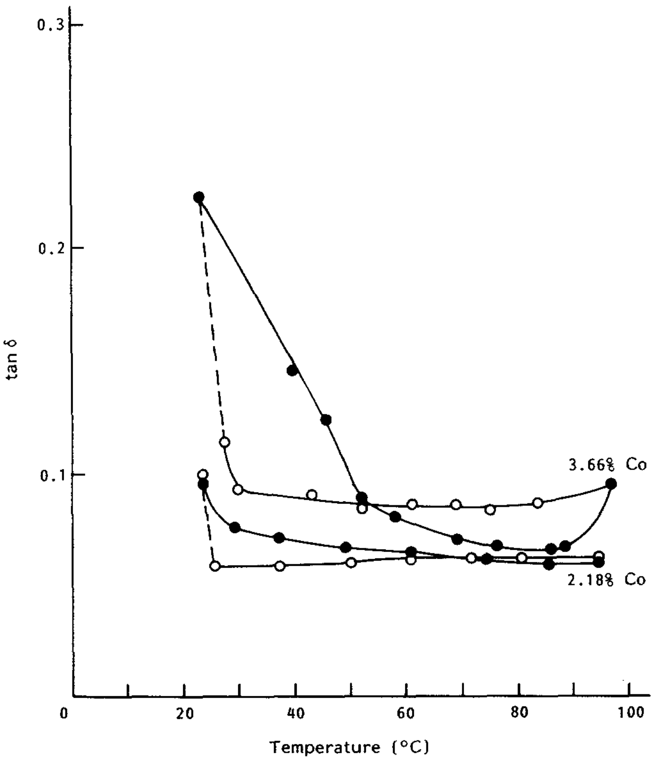

Figure 6 Semilogarithmic plots of tan δ vs. temperature for $CoCl_2$·MDA doped polyimide films at 10 MHz; (●) heat ramp, (○) cool ramp

The ambient values of tan δ for the respective films (2.18% and 3.66% doping) are ~0.10 and 0.22. Upon warming, the tan δ value drops rapidly to ~0.06 and 0.08, respectively, through the heat ramp. Once heating is removed and the sample is allowed to cool to ambient temperature, the tan δ values remain fairly constant over the duration of cooling. However, tan δ of the sample rises to a much larger value after it was left at room temperature for about 15 h after completion of the heat–cool cycle, as indicated by the broken lines in *Figure 6*. These observations suggest that the large drop in tan δ during the heat ramp is most likely due to the evaporation of moisture absorbed by the doped films. The uptake of moisture by the undoped film would be expected to be negligible, as found in previous studies[7].

CONCLUSIONS

The a.c. behaviour of cobalt-doped polyimide films has been evaluated. As expected, ε and tan δ are affected by the presence of dopant, the extent being dictated by the amount of dopant in the film. There is an apparent threshold level of doping beyond which the dielectric properties change drastically. The preliminary temperature studies indicate that these doped films actively pick up moisture, contributing to the hysteresis effect on dielectric properties of doped films. This study has shown the usefulness of a.c. measurements in evaluating such systems, and we hope to apply this method to doped polyimide films that are more conductive.

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