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Capacitance Measurements and AC Conductivity of Nickel Phthalocyanine Films

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Abstract :

AC dark Current measurements of nickel phthalocyanine thin films using ohmic gold electrodes are investigated in the frequency range 30-10⁵ Hz and within the temperature range 295-385 K. The AC conductivity as $\sigma_{AC}(\omega)$ is found to vary as ω^s within the index $s \leq 1$, indicating a dominant hopping process at low temperatures. From the temperature dependence of AC conductivity, free carrier conduction with mean activation energy of 0.31 eV is observed at higher temperatures. Capacitance and loss tangent are found to decrease with increasing frequency and increase with increasing temperature. Such characteristics are found to be in good qualitative agreement with existing equivalent circuit model assuming ohmic contacts.

Keywords: AC Conductivity; Nickel phthalocyanine ; Dielectric measurements

1. Introduction

In recent years the semiconducting and photoconducting properties of organic materials such as phthalocyanines, have received increasing attention because of their potential to replace inorganic semiconductors in the development of less expensive solar cells [1,2]. Nickel phthalocyanine (NiPc) being thermally and chemically stable, has been used as an interesting material from biological and chemical points of view. In addition, it shows a relatively high photoconductivity and electrical conductivity compared to other metalophthalocyanines [2,3].

The DC electrical properties of phthalocyanines have received the greatest attention in the form of both single crystals [4] and thin films [5,6]. On the other hand, the AC electrical properties have received considerable less attention [7], with most work to date focusing on metal - substituted phthalocyanines , such as

metal - free phthalocyanine, H₂Pc [7], copper phthalocyanine, CuPc[8], zinc phthalocyanine, ZnPc [9] and molybdenum phthalocyanine MoPc [10].

The behavior of the AC conductivity, σ_{AC} , in various phthalocyanine films was ascribed to the inhomogeneity within the solid caused by the absence of long - range crystalline order [7]. Carrier transport via a hopping mechanism was identified with this type of dielectric response [11], and Jonscher [12] has proposed that such a dependence represents a universal law, applicable to a very wide materials irrespective of their chemical and physical structure and the type of dominant charge carrier.

Measurements of capacitance and loss tangent as a function of temperature and frequency have been performed on CoPc [13,14], CuPc [8] and ZnPc films [9]. Generally, it was observed that the capacitance decreases with increasing frequency and increases with increasing temperature; this was interpreted using existing theory, for the case of a thermally activated process when using ohmic contacts [13].

In the present work, the AC conductivity, σ_{AC} , capacitance, C, and loss tangent, $\tan \delta$, in purified α - NiPc thin films have been studied over a wide range of temperature (295-385 K) and frequency (30-10⁵ Hz).

2. Experimental

The powdered NiPc obtained from Eastman Kodak Ltd. NY, was purified two times by the train sublimation technique using the method described previously [15]. The infrared spectra were found to be in good agreement with those reported by Sidorov et al. [16] over the range 700 – 3500 cm⁻¹ indicating the α - phase material. However, the α - phase is metastable and obtained either as polycrystalline powder or as a thin film deposited at temperature less than approximately 573 K [17]. The α - NiPc layer was deposited by thermal evaporation from a molybdenum boat at pressure $\leq 10^{-5}$ Pa onto precleaned glass substrates coated with an evaporated gold (Au) electrode. The deposition rate was about 5nm / min and the thickness of NiPc film ranged from 2 to 3 μ m. The resulting films were dried at room temperature in atmospheric pressure for 24 h before the deposition of the top Au electrode. The completed devices had an active area of $\approx 10^{-4}$ m². The electrical contacts were equipped with copper wires mechanically applied to the metal electrodes of the specimen using "Radio spares"

thermosetting silver paint.

To investigate the electrical properties a phase detector technique (lock - in amplifier, Stanford type SR 510) was used. The specimen was placed in a holder specially designed to minimize stray capacitance. The temperature was measured using a NiCr-NiAl thermocouple mounted in close proximity to the sample of interest, which could be read out on a Keithley 871 digital thermometer display.

3. Results and Discussion

The capacitance of NiPc films as a function of frequency, f , is measured at different temperatures. Fig. 1 shows the results for a sample of thickness $2.5 \mu\text{m}$. It can be seen from this figure that the capacitance is frequency dependent at relatively high temperatures and low frequencies, approaching a constant value at higher frequencies irrespective of temperature. Similar results have been obtained for thin films for CuPc [8], ZnPc[9], MoPc [10], H₂Pc[7] as well as pellets of CoPc [18]. These results were adequately interpreted in terms of an equivalent circuit model proposed by Goswami and Goswami [19] which has been invoked to explain the AC characteristics of CuPc films with Au electrodes [8]. Since the Au electrodes are ohmic they do not give rise to Schottky barriers and are thus represented in the model by a small series resistance, r . The dielectric layer is represented by a frequency-independent capacitive element C' in parallel with a temperature-dependent resistive element R . According to this model the measured

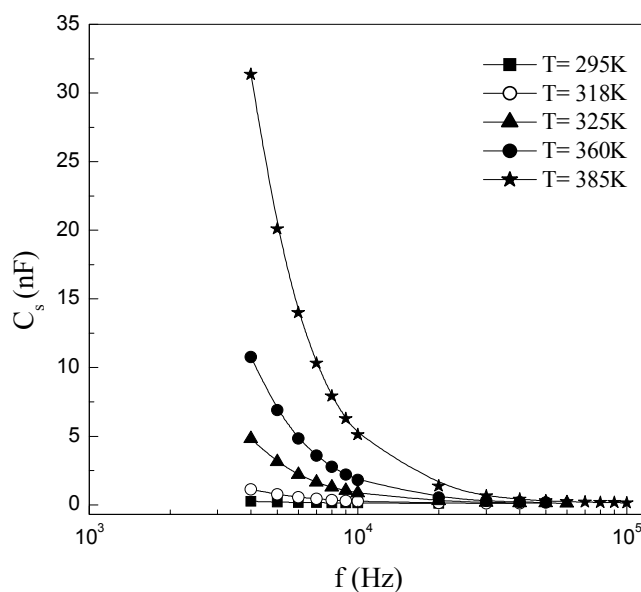


Fig. 1. Capacitance dependence of frequency at different temperatures.

series capacitance, C_s , is given by

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

and the loss tangent by

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

where ω is the angular frequency. Eq. (1) Predicts that C_s should decrease with increasing ω eventually tending to a constant value C' for all temperatures and for $\omega \geq 2.5 \times 10^5 \text{ s}^{-1}$. On the other hand C_s increased with increasing temperature as the result of decreasing R . All of these effects are clearly observed in Fig.1. The expression of $\tan \delta$ (Eq. (2)) predicts a decrease in $\tan \delta$ with increasing ω where the term ω^{-1} is dominant for lower frequencies, followed by a loss minimum at $\omega_{\min} \approx 1/[C'(rR)^{1/2}]$ [1,6] and finally to increase with ω above ω_{\min} where the term in ω is dominant.

The variation of $\tan \delta$ with frequency at various temperatures is represented in Fig. 2. The decrease of $\tan \delta$ with frequency is clearly evident as predicted for low frequencies and no indication of a minimum is observed over the frequency

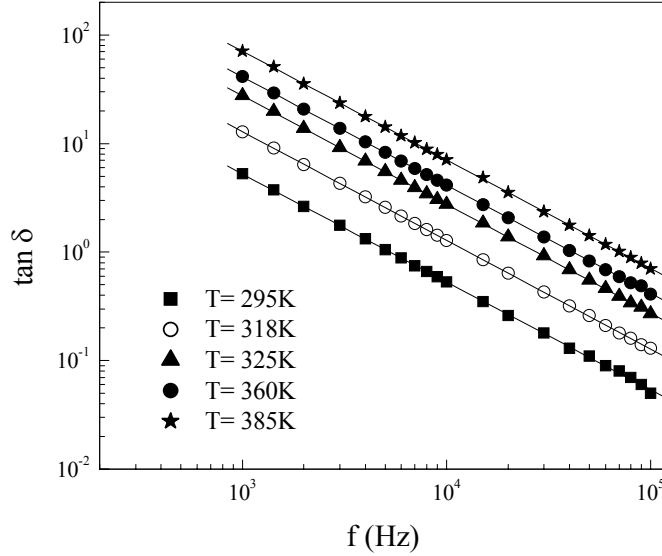


Fig. 2 Dependence of loss tangent on frequency at different temperatures

range investigated. However, further work is aimed at extending the measurements to higher frequencies and temperatures employed in an attempt to observe well-defined minima in $\tan \delta$ as predicted by the model of Goswami and Goswami [19]. It is also hoped to investigate dielectric losses at very low frequencies in other organic materials. On the other hand, it can be seen from Fig. 2 that $\tan \delta$ increases with the increase of temperature at all frequencies. The increase in $\tan \delta$ with temperature is consistent with Eq. (2) as the ω^{-1} term becomes dominant because of the decreasing value of R with temperature.

The frequency dependence of the AC conductivity ($\sigma_{AC} = \sigma - \sigma_{DC}$) for different values of temperatures is shown in Fig. 3. The conductivity obeyed the empirical law of frequency dependence given by the power law of the form [8,20]:

$$\sigma_{AC}(\omega) = A\omega^s \quad (3)$$

the variation of the exponent s with temperature gives information on the specific mechanism involved. As can be seen from Fig. 3, the value of s was found to decrease from 0.55 to 0.45 with increasing the temperature from 295 to 325 K. At high temperatures the conductivity becomes almost frequency independent over the frequency range of interest. In the case of the transport processes in disordered media [21], the low-frequency conductivity has the same frequency dependence as

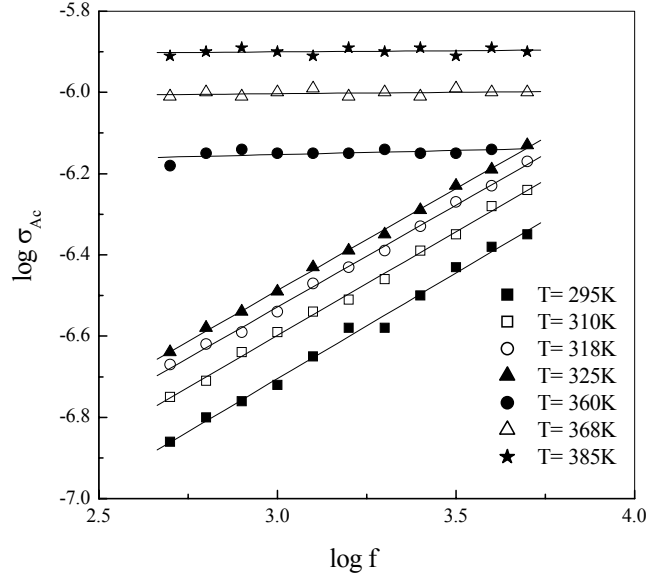


Fig.3 Dependence of frequency on the AC conductivity at different temperatures.

observed in the NiPc films, which characterizes a hopping mechanism of conduction [22]. This view is found in high purity H₂Pc [7] where σ_{AC} was measured and the hopping mechanism of the charge carrier transport was uncritically concluded, while there is no other evidence to support such a statement and often there is ample evidence that cannot be the case. However, AC conductivity having a frequency dependence in the form of Eq. (3), where $s \leq 1$, has been observed in many noncrystalline materials [8]. Abkowitz et al. [23] observed a similar sublinear frequency- dependent conductivity for both crystalline and amorphous As₂S₃ and have associated this behavior with the displacement of charge in localized electronic states, resulting from defects, impurities or internal micro- interfaces. Polycrystalline H₂Pc [7] as well as crystalline anthracence [23] have also been shown to exhibit a similar type of frequency- dependent conductivity. James et al. [10], for example, have observed an index of approximately 0.9 in MoPc films at room temperature. On the contrary, Blagodarov et al. [24] have noticed a very weak frequency dependence of the σ_{AC} of H₂Pc thin films that disappeared when a constant voltage was applied across the films. They ascribe such an effect to the domination of a band conduction mechanism in this case.

The electrical conductivity σ_{AC} as a function of temperature at constant frequency is given by [2,12]:

$$\sigma_{AC} = B \exp(-E_c / kT) \quad (4)$$

where B is constant and E_c the activation energy for conduction. The semilogarithmic relation of Eq. (4) for different frequencies are shown in Fig. 4. This figure illustrates that σ_{AC} is dependent on the frequency below approximately 325 K and is associated with very low- activation energies. Such behavior has previously been ascribed to conduction by hopping of charge carriers between localized states in various inorganic materials [26] as well as ZnPc[9], CuPc [8], H₂Pc [7] and iron phthalocyanine, FePc [27].

At temperature above 325 K, the conductivity becomes progressively frequency independent but increases more rapidly with temperature. This variation in the conductivity may be caused by charge transport through extended energy bands [8]. The values of E_c calculated from Eq. (4) is essentially independent of frequency and of a value = 0.31 ± 0.03 eV. This value is in good agreement with the values of 0.30, 0.29 and 0.33 eV reported by Gould et al. [8], Saleh et al. [2] and by Riad et al. [7] for CuPc, ZnPc and H₂Pc, respectively, and may therefore also be associated with impurities such as oxygen molecules that behave as

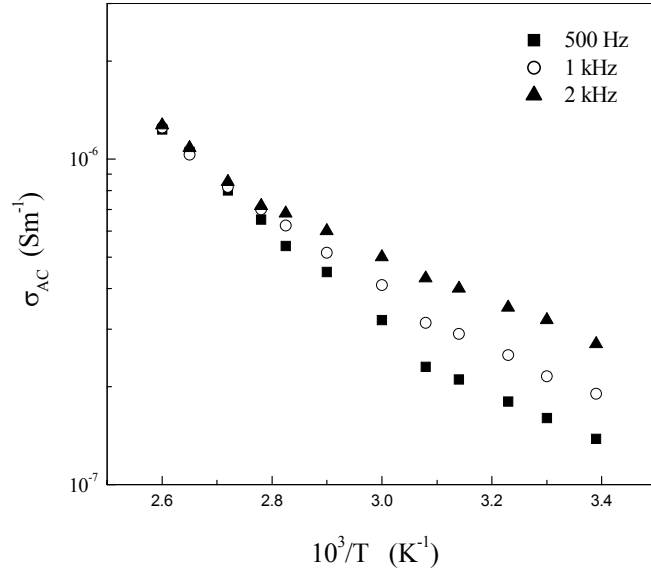


Fig. 4 Semilogarithmic plot of AC conductivity against reciprocal of temperature at three different frequencies.

acceptor levels situated above the valence band edge [9]. Such impurities are expected to give rise to carriers and free band conductivity in the temperature range of 325-385 K. However, a great number of localized states is expected to exist in NiPc but their density is incapable of dominating the statistics.

Fig. 5 shows a plot of $\log \sigma_{DC}$ versus $1/T$ of NiPc films. The slope of this curves gives $E = 0.28 \pm 0.02$ eV, while the intercept gives 5.8×10^{-3} Sm⁻¹. Therefore, it is clear that the activation energy value for σ_{AC} at high-temperature range, is close to that for σ_{DC} (within the experimental error), indicating that σ_{AC} is mainly determined by the temperature since free-carrier conduction became dominant. On the other hand, the disagreement between the activation energy value of σ_{AC} at lower temperature and that for σ_{DC} suggested that the hopping mechanism plays an important role for the conduction process in the AC measurements. Therefore, the activation energy for σ_{AC} required for the hopping mechanism in the NiPc films is assumed to be quite low.

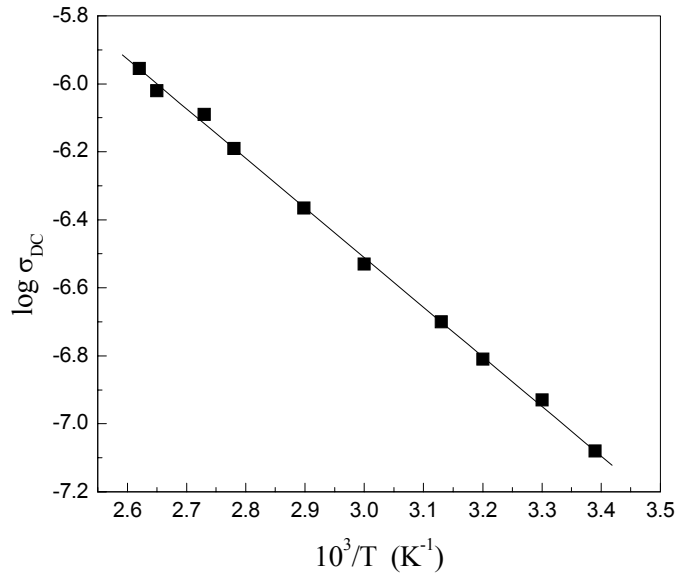


Fig. 5 Temperature dependence of DC conductivity.

4. Summary and conclusions

α - NiPc thin films sandwiched between gold electrodes have shown similar AC conductivity and dynamic characteristics as found in some other metal phthalocyanine materials. The AC conductivity generally shows a $\sigma_{AC}(\omega) \propto \omega^s$ dependence where $s \leq 1$, indicating that hopping is the predominant conduction process at lower temperatures. At higher temperatures, a thermally-activated free band process with a mean activation energy of ≈ 0.31 eV is observed. Both capacitance and loss tangent decreased with increasing frequency and increase with increasing temperature. Such behavior has been shown to be in qualitative agreement with the model of Goswami and Goswami.

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