Electrical Properties of Evaporated Thin Films of Copper Phthalocyanine

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The electrical properties of evaporated thin films of copper phthalocyanine(CuPc) were investigated by the ac method. The frequency dependence of conductivity and capacitance, and the activation energy for dc conductivity in α- and β-CuPc were determined. No significant variation in the electrical properties was observed with the difference in the phases of CuPc films *in vacuo*. The frequency dependence of conductivity and capacitance can be explained in terms of the simultaneous hopping and band conduction, *viz.*, $\sigma=\sigma_{dc}+A_1\cdot\omega^n$ and $C=C_\infty+A_2\cdot\omega^{1-n}$. The energy gap for α- and β-CuPc *in vacuo* is 1.80 eV and 1.89 eV, respectively. The adsorbed O_2 gas has a great effect on the dc conductivity but little on the ac conductivity of α-CuPc film. The adsorption of oxygen on α-phase CuPc might be the cause of high dc conductivity and low activation energy(0.5—0.7 eV) as compared with those *in vacuo*.

It is known that copper phthalocyanine(CuPc) can be obtained in two crystallographic modifications(α and β). Wihksne and Newkirk[1] found that the conductivity of form α is greater than that of form β by a factor of 10^5, the activation energies being 0.25 eV and 0.9 eV, respectively. On the other hand, Harrison and Ludewig[2] claimed that the difference in conductivity is due to the greater adsorptivity for oxygen on α-phase CuPc, and found that the conductivity of the α-phase film is similar to that of the β-phase one when the oxygen has been eliminated. Eley and Parfitt[3] studied the ac conductivity of aromatic compounds. They explained the frequency dependence of conductivity in a compressed powder disk in terms of contact resistance and contact capacitance(Maxwell-Wagner type dispersion). The frequency dependence of the conductivity in aromatic compounds can be explained in terms of the hopping conduction mechanism rather than the Maxwell-Wagner type dispersion.[4,5] We have studied the frequency and temperature dependence of conductivity as well as the capacitance of α- and β-phase CuPc films.

Experimental

Electrical measurements were carried out on evaporated thin α- and β-phase CuPc films, the surface of the film being expected to be in alignment with its *ab*-plane. An ac bridge TR 10C(Ando Electrics Co., Ltd.) was used to measure the conductivity and capacitance. The sample was held in O_2 or H_2 atmosphere or *in vacuo*(about 10^{-2} Torr). A sandwich type cell of thin film was prepared by evaporation on a microscope slide. The evaporation was carried out in a vacuum of the order of 10^{-6} Torr, the rate of deposition of CuPc being approximately 10^{-7} mm/s. The bottom electrode was an evaporated silver layer covered with an evaporated thin film of CuPc. The CuPc thickness was about 10^{-3} mm. The top electrode was also prepared by the evaporation of silver. The cell constant was determined to be about 2×10^3 cm. The β-phase CuPc was obtained by annealing the evaporated film at 320 °C for 30 min in N_2 atmosphere.[1,2] The transition from α to β-phase on annealing was confirmed by the IR spectrum of the CuPc film which was deposited on a KBr disk. This was also confirmed by the change of electrical conductivity, the result being similar to that obtained by Wihksne and Newkirk[1] as well as by Harrison and Ludewig.[2] Measurements of the conductivity and the capacitance were carried out at temperatures 13—130 °C (±2 °C). The frequency was varied from 30 Hz to 1 MHz. The amplitude of the alternating voltage amounted to 20 V.

Results and Discussion

Ebert and Gottlieb[6] studied the X-ray diffraction and IR spectra of α- and β-CuPc. Their results indicate that the IR spectrum of α-CuPc differs from that of β-CuPc at the wavelengths 7.6, 9.2, 11.4, 13 and 14 μm. The spectra of the deposited CuPc film on a KBr disk and the annealed one were found to be similar to those obtained by Ebert and Gottlieb, indicating that the evaporated film of CuPc on a slide glass is in the α-phase while the annealed one is in the β-phase.[2]

The frequency dependence of conductivity for the α- and β-CuPc films *in vacuo* at various temperatures is shown in Figs. 1 and 2. The temperature and the frequency dependences of the electrical properties for both α- and β-CuPc *in vacuo* were found to be similar, indicating that there is no significant difference between the two phases. In the high frequency region, it was found that the conductivity of both α- and β-CuPc is proportional to ω^n:

$$\sigma_{ac} = A_1\cdot\omega^n \tag{1}$$

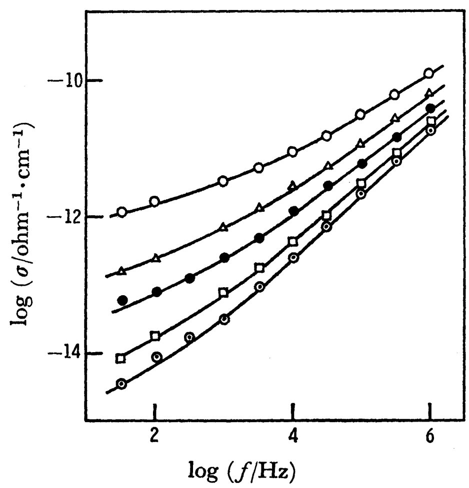

Fig. 1. Frequency dependence of conductivity of α-CuPc film *in vacuo*.
(○) 124 °C, (△) 98 °C, (●) 74 °C, (□) 47 °C, (⊙) 27 °C.

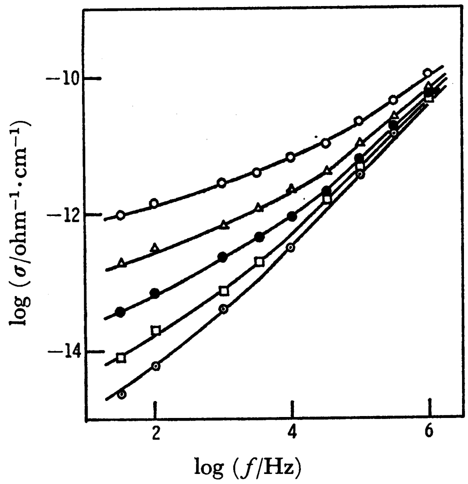

Fig. 2. Frequency dependence of conductivity of β-CuPc film *in uacuo*.
(○) 127 °C, (△) 99 °C, (●) 76 °C, (□) 45 °C, (⊙) 18 °C.

where ω is the angular frequency. The value of n decreases from 1.0 to 0.5 with an increase in temperature. σ_{ac} at low frequencies was calculated by extrapolation from the high frequency region on the assumption that σ_{ac} obeys Eq. (1) over the whole range of frequency. In the low frequency region the difference between σ_{ac} value thus obtained and the observed conductivity increases with an increase in temperature.

We have studied the frequency and temperature dependence of conductivity of aromatic compounds in both an evaporated thin film and a compressed powder disk and have found that the observed conductivity can be expressed as the sum of two terms, the band conduction and the hopping conduction.[4,5] The latter strongly depends on frequency, but not the former. Thus we have

$$\sigma = \sigma_{ac} + \sigma_{dc}$$
$$= A\cdot\omega^n\cdot\exp[-E(T\cdot\omega)/kT] + \sigma_0\cdot\exp(-E/kT) \quad (2)$$

where σ_{ac} is the frequency dependent conductivity, σ_{dc} is the frequency independent conductivity, $E(T\cdot\omega)$, the apparent activation energy for hopping from one localized state to another, is a function of both temperature[7-9] and frequency, and E is the activation energy of the band conduction. When the conductivity is given by Eq. (2), the Kramers-Kronig relation[10] can be used to determine the frequency dependence of the capacitance:

$$C = C_\infty + A_2\cdot\omega^{1-n} \quad (3)$$

The values of n for conductivity and capacitance were obtained at various temperatures by use of Eqs. (2) and (3). It was assumed that C_∞ is roughly equal to the value of C at 1MHz. The values of n thus obtained are given in Table 1. The values of n in C are in fair agreement with those in σ_{ac}. The results indicate that the frequency dependence of conductivity and capacitance can be expressed by Eqs. (2) and (3) within experimental error. We see that σ_{ac} of α-CuPc and that of β-CuPc do not differ greatly (Fig. 3). The apparent activation energy of ac conductivity decreases with the increase in frequency and the decrease in temperature for both α- and β-CuPc *in vacuo*.

Table 1. Values of n for α-CuPc and β-CuPc films *in vacuo* and in H_2 atmosphere

Phase	Temp. °C	n in σ_{ac}	n in C
β *in vacuo*	127	0.4_9	0.5_2
	99	0.5_4	0.5_7
	76	0.6_8	0.6_4
	45	0.8_3	—
α *in vacuo*	124	0.5_0	0.5_7
	98	0.6_3	0.5_9
	74	0.6_9	0.7_5
	47	0.8_1	0.7_6
	27	0.8_3	0.7_6
α in H_2	122	0.5_0	0.5_0
	99	0.5_5	0.5_4
	73	0.6_5	0.5_9
	54	0.7_2	0.6_6
	31	0.8_4	—

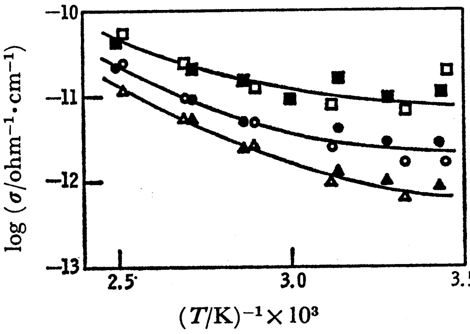

Fig. 3. Temperature dependence of conductivity in the high frequency region of α- and β-CuPc films *in vacuo*.
(□, ○, △) α-CuPc, (■, ●, ▲) β-CuPc, (□, ■) 300 kHz, (○, ●) 100 kHz, (△, ▲) 30 kHz.

The temperature dependence of σ_{dc} $(=\sigma - A_1\cdot\omega^n)$ was obtained for both α- and β-CuPc (Fig. 4). The activation energy of σ_{dc} is 0.90 eV and 0.94 eV for the α-CuPc and the β-CuPc film *in vacuo*, respectively. These are in fair agreement with those obtained by Harrison and Ludewig.[2]

The effect of adsorbed O_2 gas on the electrical properties was investigated. The frequency dependence of conductivity for α-CuPc film in H_2 and O_2 is shown in Figs. 5 and 6. The frequency dependence of conductivity and capacitance in H_2 is similar to that *in vacuo* (Table 1) but the activation energy of dc conductivity is slightly larger than that *in vacuo*. In the low frequency range, the conductivity of α-CuPc in O_2 is larger than that *in vacuo* by a factor of 10^4 at room temperature. The magnitude of σ_{dc} was poorly reproducible, being strongly affected by the condition of O_2 gas adsorption. The activation energy was found to be 0.5—0.7 eV. When the contribution of σ_{dc} component is large, the frequency dependence of σ_{ac} can be obtained by subtracting σ_{dc} from σ on the assumption that the value of σ_{dc} is approximately equal to that of σ in the low

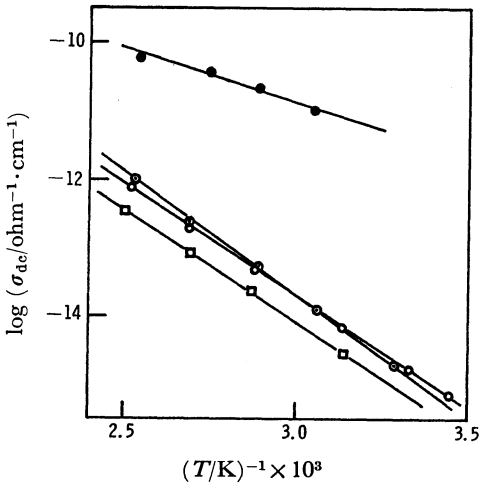

Fig. 4. Temperature dependence of dc conductivity of CuPc film in various conditions.
(□) β-CuPc film *in vacuo*, (○) α-CuPc film *in vacuo*, (⊙) α-CuPc film in H_2 atmosphere, (●) α-CuPc film in O_2 atmosphere.

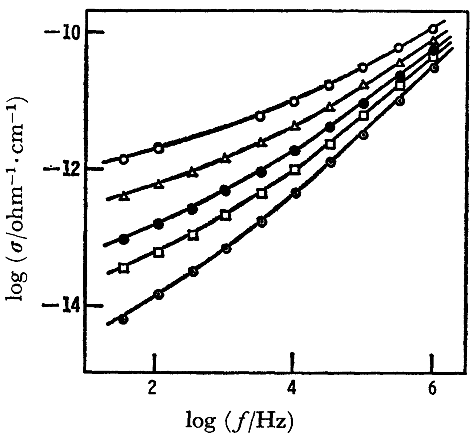

Fig. 5. Frequency dependence of conductivity of α-CuPc film in H_2 atmosphere.
(○) 122 °C, (△) 99 °C, (●) 73 °C, (□) 54 °C, (⊙) 31 °C.

frequency region. The frequency dependence of σ_{ac} is shown in Fig. 7. It can thus be said that the σ_{ac} is little affected by the adsorbed O_2.

The band conduction σ_{dc} becomes gradually predominant at low frequency range with temperature rise, so that in the high temperature region the conductivity depends little on the frequency. Such a remarkable tendency is observed in particular in α-CuPc under O_2 atmosphere. It seems that the hopping conduction σ_{ac} is mainly based on the localized state (and/or shallow traps) which might be produced by crystal

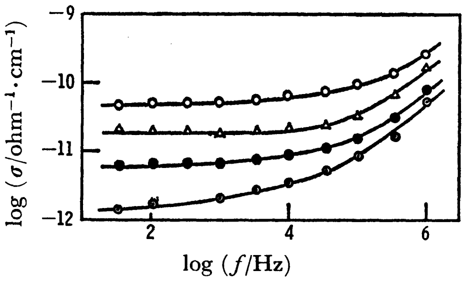

Fig. 6. Frequency dependence of conductivity of α-CuPc in O_2 atmosphere.
(○) 120 °C, (△) 74 °C, (●) 55 °C, (⊙) 34 °C.

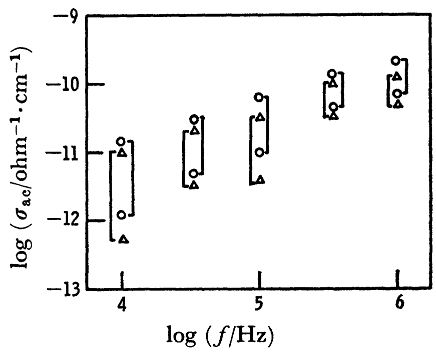

Fig. 7. Frequency dependence of σ_{ac} of α-CuPc films.
(○) in O_2 introduced after evacuation,
(△) in H_2 atmosphere.

defects but not adsorbed oxygen, and the band conduction σ_{dc} is due to electrons excited to the conduction band and/or holes to the valence band. Since the frequency at which traps produced by adsorbed oxygen are filled and emptied is greater than the applied field frequencies, the adsorbed oxygen has no effect on thermally and frequency assisted hopping conduction.

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