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Density-of-States Function in Metal-Free Phthalocyanine: Effect of Exposure to Chlorodifluoromethane

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Summary: Changes in the energy structure of local states during the exposure of metal-free phthalocyanine films to chlorodifluoromethane were studied using the technique of thermomodulated space-charge-limited currents. The broadening of the energy distribution of the states is explained on the basis of charge-dipole interactions.

Keywords: chlorodifluoromethane; electron-dipole interaction; gas sensing; local states; phthalocyanine

Introduction

Phthalocyanines have been known for many years as organic semiconductors[1]. Among many possibilities of their applications as organic metals, photoconductors, solar cells, non-linear optical media, light limitators, electroluminescent diodes, optical data storage devices, and photosensitizers[2] is also gas sensing. Due to formation of charge-transfer species[3,4], phthalocyanines change their electrical conductivities over several orders of magnitude upon exposure to BF_3, BCl_2, F_2, Cl_2, I_2, NO, NO_2, O_2, and other gases[5,6]. However, the changes in capacitance, optical absorption, and optical refractivity can also be used for gas detection. These changes usually reflect the variations in the energy structure of the sensing material. It was found that polar dopants broaden the distribution of the transport hopping states due to electron-dipole interaction[7,8]. One can also expect a similar influence of some gases on deeper local states.

In this paper we describe changes in the energy structure of local states upon exposure of metal-free phthalocyanine (H_2Pc) films to polar chlorodifluoromethane ($CHClF_2$). Two methods were

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used in the study: temperature dependence of the DC electrical conductivity and thermomodulated space-charge-limited current (TM-SCLC) spectroscopy.

Experimental

H_2Pc was purified by sublimation in a temperature gradient. Gold coplanar electrodes, separated by 0.7 mm and 13 μm gaps for the measurements of the tempearture dependence of electrical conductivity and TM-SCLC, respectively, were deposited on Corning 7059 glass substrates. Thin (100 ÷ 150 nm) H_2Pc films were deposited on the electrode system by vacuum evaporation; the deposition rate was 15 nm min^{-1}. The presence of the α-form of H_2Pc after the evaporation was checked by UV-VIS and IR spectroscopies[9,10].

After mounting a sample in the measuring chamber, the system was evacuated to a pressure of 7 Pa and then filled with nitrogen (purity 99.996 %) to atmospheric pressure. This procedure was repeated three times. $CHClF_2$ was applied into the chamber through a rubber membrane by injection. In this way $N_2 - CHClF_2$ mixtures were prepared, with the concentration of the latter ranging between 60 and 500 ppm.

Electrical conductivity was measured using a Keithley 617 electrometer. The samples for the TM-SCLC measurements were first heated in N_2 atmosphere to 140 °C with the aim to desorb oxygen. Then TM-SCLC characteristics, i.e. current (I) vs. voltage (U) and activation energy of the current (E_a) vs. U dependences were measured at room temperature (temperature modulation $\Delta T = 6$ °C). After the $CHClF_2$ exposure, the sample was heated again to 140 °C and then slowly cooled (8 h in the dark) to room temperature. The energy spectrum of density-of-states (DOS) function $h(E)$ was constructed from the TM-SCLC characteristics using the procedure described in Ref.[11].

Outline of the TM-SCLC theory

For any position of the energy of the Fermi level E_F, the equation is fulfilled

$$E_F(L) = -kT \ln \frac{I}{U} \chi_1 + C \qquad (1)$$

where $C = kT \ln(e\mu_0 N_b / L)$, L is the sample thickness (the charge injection is realized by a contact at coordinate $x = 0$), k is the Boltzmann constant, T is temperature, e is the elementary charge, μ_0 is the charge carier mobility, N_b is the effective density of states, and χ_1 is parameter of the order of unity whose exact relation to experimental variables is $\chi_1 = 1/(2 - \gamma)$, where $\gamma = d(\ln U)/d(\ln j)$ is the slope of the U-I characteristic.

The total concentration of the charge carriers (n_s) (in most cases practically equal to the concentration of the trapped carriers) is given by the equation

$$n_s = \int_E h(E) f(E - E_f) \mathrm{d}E = \frac{\varepsilon\varepsilon_0}{eL^2}(2-\gamma)(1-\gamma)(1+B)U \tag{2}$$

where $h(E)$ is the density-of-states (DOS) function to be determined, f is the Fermi function, $\varepsilon\varepsilon_0$ is the electric permittivity and B is a term containing higher-order corrections.

Changing the voltage V, E_F moves from its "thermodynamic" value towards the extended states scanning the local states by changing their occupancy

$$\frac{\mathrm{d}n_s}{\mathrm{d}E_f} = \frac{\mathrm{d}}{\mathrm{d}E_f}\left(\int_E n_s(E)\mathrm{d}E\right) = \int_E h(E)\frac{\mathrm{d}f(E-E_f)}{\mathrm{d}(E-E_f)}\mathrm{d}E \tag{3}$$

The increment of the space charge due to the shift of the Fermi level $\mathrm{d}n/\mathrm{d}E_F$ is connected to the experimentally measured data via Eqs. 1 and 2. The DOS function $h(E)$ is obtained after deconvolution of the integral in (3) as

$$h(E) = \frac{\mathrm{d}n_s}{\mathrm{d}E_f}\left[1 - M_2\left(a^2 + a'\right)\right] \tag{4}$$

where

$$M_2 = \int_{-\infty}^{+\infty} (E_f - E)^2 f(E-E_f)[1 - f(E-E_f)]\mathrm{d}E = 3.2898(kT)^2 \tag{5}$$

and $a = \mathrm{d}(\ln \mathrm{d}n_s/\mathrm{d}E_f)/\mathrm{d}E_f$ and $a' = \mathrm{d}a/\mathrm{d}E_f$.

The energy scale can be determined using a dominant energy level E_d. Mathematically, E_d represents the first momentum of the energy distribution of trapped carriers

$$E_d = \frac{\int_E h(E)(E_v - E) f(1-f)\mathrm{d}E}{\int_E h(E) f(1-f)\mathrm{d}E} \tag{6}$$

E_d can be determined from the experimental data as

$$E_{\mathrm{d}} = E_{\mathrm{a}} + \frac{(3\gamma-4)\gamma}{(2-\gamma)(1-\gamma)}\frac{\mathrm{d}E_{\mathrm{a}}}{\mathrm{d}(\ln I)} + \frac{1}{1+B}\frac{\mathrm{d}B}{\mathrm{d}(1/kT)} \tag{7}$$

where E_a is the experimentally measured activation energy of the SCL current determined from the relation $I = I_0 \exp(-E_a/kT)$.

Results and discussion

Temperature dependences of the electrical conductivity

Temperature dependences of the dc electrical conductivity (*S*) are plotted in Figure 1. Curve 1 was measured in $CHClF_2$ atmosphere. The log *S* vs. 1/*T* dependence can be approximated with a stright line, with the activation energy E_a = 0.66 eV. Curve 2 was measured on increasing the temperature after replacing $CHClF_2$ with N_2. The non-Arrhenius part of the curve at elevated temperatures can be associated with the desorption of $CHClF_2$. Curve 3 was measured in N_2 atmosphere, E_a = 0.91 eV.

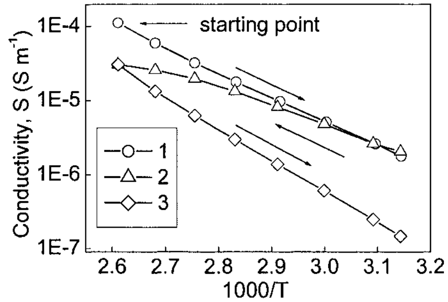

Figure 1. Temperature dependences of the dark conductivity. Curve 1 – in $CHClF_2$ atmosphere, *T* decreasing, 2 – in N_2, *T* increasing, 3 – in N_2, *T* decreasing

Thermomodulated SCLC spectroscopy

The TM-SCLC characteristics, i.e. *I* vs. *U* (a) and E_a vs. *U* (b) are presented in Figure 2. The low-voltage part of the *I*-*U* characteristic is quadratic followed by a superquadratic one at voltages exceeding 5 V. As follows from the E_a - *U* characteristics, the shift of the Fermi level during a voltage run in N_2 atmosphere is expected to be from about 0.8 eV to 0.2 eV.

Generally, the slopes of the *I* - *U* characteristics in the voltage range 5 – 50 V decrease with increasing $CHClF_2$ concentration, as does the low-voltage activation energy. The set of curves presented in Figure 2 allows to construct the DOS function (see Figure 3). Four peaks, with maxima at 0.26, 0.32, 0.40, and 0.52 eV and low-energy tail states were detetected. The trap 0.52 eV deep is often attributed to oxygen Coulombic centres for holes[6,12]. Traps in the energy interval (0.3 - 0.4) eV have been reported in the literature[13,14]; they are usually characterized as structural ones. Their concentration and energy depend on, e.g., the rate of the film deposition[13,14,15]. Our experiments reveal the presence of two peaks in this energy range; at present we cannot decide whether the doubling is a real phenomenon or an artifact associated with the calculation procedure we employed. The trap 0.25 eV deep was also found from steady-state photoconductivity measurements.

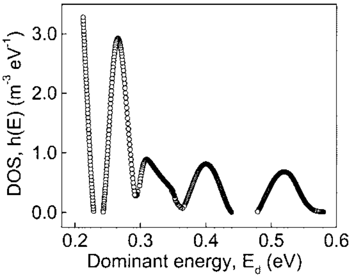

Figure 2. Energy distribution of DOS of H_2Pc film in N_2 atmosphere

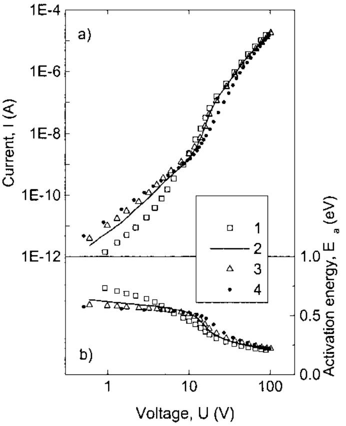

Figure 3. (a) I-U, (b) E_a-U characteristics as a function of $CHClF_2$ concentration.
1 - N_2 only, 2 - 120 ppm,
3 - 235 ppm, 4 - 470 ppm

Because of the polarity of the $CHClF_2$ molecule (dipole moment $\mu = 1.56$ D), one can expect a broadening of the trap distribution due to charge-dipole interactions[7,8]. The effect was indeed found in our experiments. The evolution of the peak at 0.26 eV with $CHClF_2$ concentration is given in Figure 4.

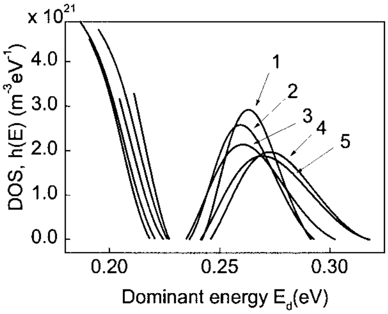

Figure 4. Broadening of the peak at 0.26 eV with increasing $CHClF_2$ concentration: Curve 1 - N_2 atmosphere, other curves N_2 – $CHClF_2$. Concentration: curve 2 - 60 ppm, curve 3 - 120 ppm, curve 4 - 175 ppm, curve 5 - 235 ppm

Two important features were observed with increasing concentration of $CHClF_2$: (i) the half-width of the peak increased, (ii) the overall concentration of local states was constant. The FWHM of the peak as a function of the $CHClF_2$ concentration is plotted in Figure 5. The broadening of the DOS function with increasing concentration of $CHClF_2$ can be explained on the basis of charge-dipole interactions[7] and it is in a good agreement with theoretical predictions[8]. Similar broadening was also observed for the deeper local states.

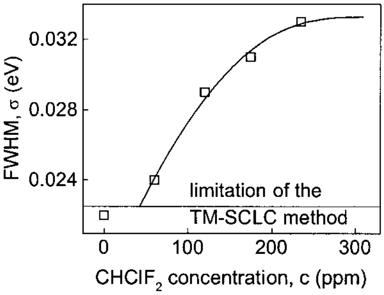

Figure 5. Dependence of FWHM of the 0.26 eV peak on the $CHClF_2$ concentration

Conclusion

The broadening of the energy distribution of local states for charge carriers was observed during the exposure of metal-free phthalocyanine films to chlorodifluoromethane. The effect is explained on the basis of charge-dipole interactions.

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