Two-component Sublimed Films Based on Phthalocyanines for Gas Analytical Applications

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Two-component film systems composed of PcCu and Cl_{16}PcCu are proposed and it is shown that certain extreme phase compositions have unusual physico-chemical properties.

Metal phthalocyanines, (PcMs) are a very convenient model for the study of the phaseous (electrical, optical, *etc.*) properties of organic solids and also the molecular structures of macroheterocyclic metal complexes.[1–10] PcMs are very versatile in directed molecular design and controlled molecular architecture studies because of their extended π-electronic system.[1–2] There are many syntheses of PcMs and they may be directed by modifying the central moiety and the macroligand.[1–2] PcMs are quasi-two-dimensional molecules forming solid bodies with quasi-one-dimensional conductivity.[1] Thin metal Pc films are currently being tested as active materials in resistive gas sensors as an electrical or acoustic method of signal detection.[2–8]

As shown previously,[3] the interaction of Hal_xPcM with NH_3 is low in energy and close to physisorption, and does not lead to substantial changes in the redox states of all members of the studied series. However, the substitution affects the ability of the PcM molecule to coordinate to molecular oxygen which is always present in real structures and mainly defines the impurity p-type conductivity of thin PcM films.[1,5,9] It follows from ref. 3 that oxygen effect compensation with the donor agent, NH_3, observed with initial PcCu films, disappears with an increase in x. This may be connected with a change of acceptor properties of the chlorinated macroligand in respect to the central metal atom. It diminishes its ability to bind molecular oxygen and increases its ability to coordinate to simple molecules such as NH_3 and H_2O.

In the next step of our investigations we chose the design of two-component systems based on PcCu and Cl_{16}PcCu which have completely different donor–acceptor and coordination properties. The systems were studied in the form of thin sublimed solid films, as we could obtain regular high-purity structures by a new method of simultaneously controlled vacuum evaporation for the deposition of PcM two-component film structures.

The technique used was d.c. conductivity measurements of PcM films; simultaneously, parallel measurements of a sorptional activity of the films using a quartz crystal microbalance (QCM)[3,4,6] were carried out. All measurements were conducted in a specially designed measuring cell built by an original technique described in ref. 4. Similar techniques and substrates have been described earlier.[3,5,6]

Two-component film structures based on PcM were first investigated by optical methods described in ref. 10. However, their preparation was not perfect, so we used composite thin film deposition, Fig. 1. Evaporation is carried out in high vacuum (*ca.* 10^{-4} Pa) from two different quartz tubes (1), which are placed in heating installation (2) at an angle of about 75° to one another. The sublimation temperature for PcCu and Cl_{16}PcCu varies (*ca.* 450–500 °C and 600–650 °C, respectively) and it was selected so that the speed of growth of the deposited film does not exceed 0.05 nm s^{-1} to ensure a good quality layer; the thickness of the films was approximately 150 nm. Two molecular flows of sublimed phthalocyanines (3) were produced, the speed of sublimation was controlled by a QCM detector (4). When a certain required ratio between the flows was established, we opened the trap (5) in the front of the target (6), which is a measuring device with an attached substrate (7). The speed of simultaneous

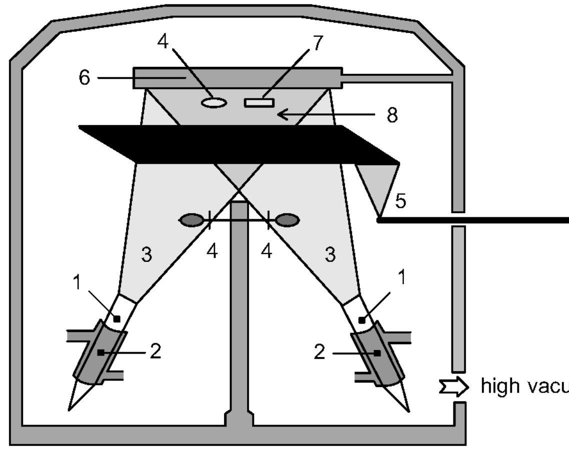

Fig. 1 Installation for the simultaneous deposition of two-component film structures by vacuum evaporation.

deposition onto the substrate introduced into the overlap area (8) (see Fig. 1) was controlled by another QCM detector (4), fixed on the table (6) near substrate (7). Both the latter detector and the substrate were used for further measurements. At a fixed flow ratio we can obtain similar layers with preservation of the original crystalline structure (in this case a-form[1,7] for both PcMs), that was confirmed by small angle X-ray analysis (compared with ref. 7) and electronic spectroscopy, but in other cases we obtained an amorphous mixture. The ratio, N(PcCu)/N(Cl_{16}PcCu), N = the number of molecules, for such films may also be confirmed by the position of the maximum of the Q-band[3,9,10] in the electronic spectrum (visible region). The position of the Q-band for the initial components differs by 33 nm; both the shift and the intensity of the studied band[10] for a mixture of these compounds are proportional to the concentration of one component in the other.

There are many studies of conductivity of PcM films with doping with metals or iodine, and observed changes have been correlated to the influence of impurity gas molecules as well as to the change of PcMs crystal structure, see *e.g.* ref. 9. Thus, the initial structure of PcM was not destroyed, and instead an element with different geometry and electron affinity was introduced into the PcM stacks.[7] This leads to an interesting result.

The phase diagram of the composition–property type was constructed, Fig. 2. Here, the initial [$P(NH_3)$ = 0] conductivity, σ_0, and the sorption value, in this case $N(NH_3)/N$(Pc), were considered as a system property. The obtained experimental dependence, curve *a*, differs from the additive one, curve *b*, by the presence of a σ_0 maximum at the ratio N(PcCu):N(Cl_{16}PcCu) = *ca.* 80:20. The conductivity of the phases (solid solutions) of this extreme composition is very sensitive to the pressure of NH_3 in respect to several PcMs: about 5–6 orders of magnitude for $P(NH_3)$ = *ca.* 29 Pa.[3] This may be connected with a definite alteration period **D**···**A**······**A**···**D** (**D** = donor, **A** = acceptor) in the generated quasi-one-dimensional chain (Fig. 2, *1*), which leads to an improved

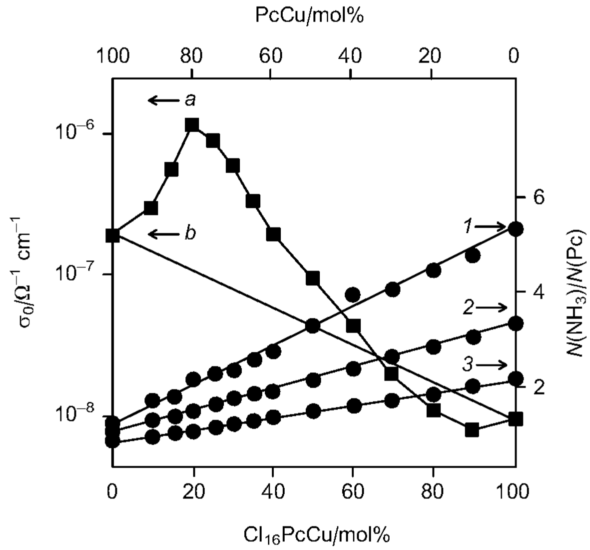

Fig. 2 The diagram 'composition–property' for a PcCu/Cl_{16}PcCu mixture: curve *a*, *b* – s_0 value (left axis), curves *1*, *2*, *3* – $N(NH_3)/N(Pc)$ value (right axis).

charge transfer across the PcM 'stacks'. To the right of Fig. 2 curve *a* is beneath the additive one *b*, which may be connected with a 'locking' role of PcCu molecules at a given concentration.[2] The interaction of strong electron-donor agents such as NO_2[8] with our systems seems interesting and worth investigating, because the cation radical forms $[Pc*M]^+$ have very high conductivity in thin solid films.[5,7,8]

The dependence of the $N(NH_3)/N(Pc)$ value on the film composition is shown in Fig. 2, curves *1*, *2* and *3* at different NH_3 pressures [*1* – 2.00, *2* – 1.33 and *3* – $P(NH_3)$ = 0.66 kPa]. The number of sorbed gas molecules, $N(NH_3)$, increases nonlinearly with a rise of $P(NH_3)$, and in coordinates $N(Pc)/N(NH_3) = f(1/P)$ this dependence corresponds to the Langmuir law. As follows from Fig. 2, at the same $P(NH_3)$ the highest sorption activity is shown by the film containing the highest amount of Cl_{16}PcCu. It also means that Cl_{16}PcCu can coordinate NH_3 molecules better as a result of the reinforced acceptor properties of the Pc-macroligand (confirmed by IR spectroscopy).

The formation of solid solutions in two-component systems seems to be one of the most interesting domains in the study of PcM film architecture from both a fundamental as well as a practical point of view.

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