

Conductivity measurements on phthalocyanine films: evaporated vs. pressure contacts

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Abstract

Conductivity measurements on thick films of lead phthalocyanine in a sandwich cell with one pressure contact are reported. The results obtained at different loads are discussed and compared with those for a cell with both evaporated contacts.

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Phthalocyanines (Pc's) represent an important class of organic molecular solids that may have a variety of applications, including devices based on thin film technology, such as OLEDs, sensors, FETs etc. [1–5]. (Photo)-electrical measurements on Pc films are commonly carried out on the so-called ‘sandwich’ (or capacitor-like) cells. A Pc film is deposited by vacuum sublimation on the bottom electrode (e.g. metal, ITO) already formed on an insulating support (glass, ceramics), and then covered with a top contact which is in most cases a thin metallic layer evaporated within the same technological cycle. Interestingly, the biggest difficulties attaining stability of such devices and the problems of their practical usage are associated with this top interface (see, e.g., [3]). Less common, the so-called comb-like (or interdigital) planar cells are employed [4,5]. Despite a clear-cut electrode pattern set by the resolution of lithography, these are not suitable, for example, for multilayered structures, for

experiments on the materials with various work function, etc. Recently, a ‘soft contact lamination’ technique was introduced in order to avoid many problems like uncertainty and instability of the interface or materials diffusion [6], but it appears to be labor-intensive still.

Meanwhile, external pressure can change the physical properties of Pc materials [7–10], in particular, increase the conductivity by 6–7 orders of magnitude. However, these data refer to powders and very high pressures [9,10], but not to the Pc films (a pressure sensor is proposed in [11]). Typically, the thickness of evaporated Pc films lies in the range of 10–1000 nm, they are known as soft, easy to damage and unsuitable for direct contacting (see, also [6]).

In this communication we briefly report on the conductivity measurements using both evaporated and pressure contacts and relatively thick Pc films with a focus on whether it is possible to compare these two types basically.

Lead phthalocyanine, PbPc (Aldrich) was chosen as a model compound since it has a somewhat higher specific conductivity compared to conventional divalent Pc materials [12–15], which allows the use of wider

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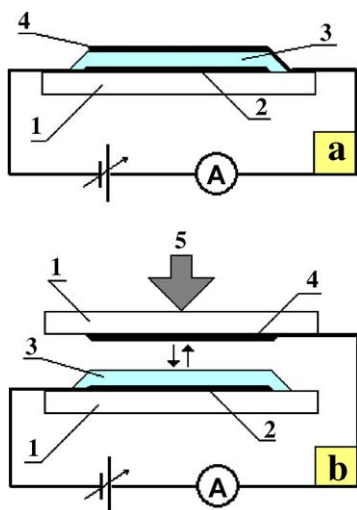


Fig. 1. Schematic of the samples: (1) ceramic plate; (2) bottom metallic contact; (3) PbPc layer; (4) top metallic contact; (5) external load.

interelectrode gaps. Besides it is responsive to pressure [7,9]. The PbPc films ca. 5 μm thick were evaporated in a VUP-5(SU) installation under vacuum ca. 10^{-4} Torr at a deposition rate of 0.2–0.6 nm/s [5]. This film thickness (one of the greatest reported), on one hand, requires a reasonable process time and allows a stable electrical signal. On the other hand, such ‘thick’ films (dark-blue, nearly black colored) are easier to handle, resistive to abrasion, perforation, etc.

The bottom contact was an indium (or gold) layer deposited on a polished ceramic (Sitall) plate 600 μm thick—Fig. 1(a) and (b). For the first series of samples (Fig. 1(a)), the second (top) electrode was immediately deposited on the surface of the PbPc film. The device area was 7 mm². Such metal/Pc/metal structures are well studied in the literature [14–20] and serve further as reference. The I/V plot in the range of 0–10 V is shown in Fig. 2 for an In/PbPc/In cell. Both the forward and reverse characteristics are nonlinear over the indicated voltage range and not completely symmetrical, especially at lower voltages—see, Fig. 2 (inset). A slower rise of current was observed at a negative bias on the top electrode. Despite the contacts in both interfaces are made of the same material, their true physical nature is different [3,14,15,17,18], which causes this asymmetry (see Table 1 for parameters). The experimental data were approximated by the typical functions describing possible situations at a metal/PbPc interface: linear, the power law dependence, diode-like behavior and the Schottky type dependence¹ [14]. For gold contacts, the best matching fits over the entire voltage range were

obtained for a linear dependence (not shown here, cf. [18–20]). For indium contacts, the power dependence was most suitable, which is shown in Table 1 along with the values of the corresponding coefficients. The value of b close to 2 suggests space charge limited conductivity (SCLC) dominated by a single trap level. It should be mentioned that for all other samples b is much less than the values commonly derived for such a regime in the Pc films (2...7) although correlating, e.g. with the data in Refs. [19,20] obtained on the assumption of SCLC. As a matter of fact, there is a large variety of models and ample data on this problem in the literature [11–20], but a detailed discussion is deliberately avoided here.

For a second series of samples, the top contact was an In coated plate (Fig. 1(b)), which was driven to the surface of a PbPc layer by a micrometric manipulator. After these two parts of the cell were brought in contact, with a special care of proper positioning, the I/V dependencies were measured—Fig. 3, Table 1. As expected, the overall resistance of such cells was much higher than that of their evaporated counterparts due to, say, ‘bad’ contact or additional series resistance (cf. Fig. 2).

Afterwards, the top electrode was loaded successively with two weights, so that the uniaxial pressure of 0.8 and 1.9 MPa was applied to the cell, and data were taken—Fig. 3, Table 1. The asymmetry of the forward/reverse I/V plots in this case is feebly marked. The profile of the dependencies becomes, however, different: the conductivity in both directions now obeys the $J=a(e^{bU}-1)$ equation which can be associated with a Schottky type conductivity assuming $a=J_s$, a reverse saturation current, and $b=e/nkT$ (all symbols have the usual meaning [14]). The power coefficient b in this equation does not change with an increasing pressure, the changes in conductivity are mainly due to the pre-exponential factor a —Table 1, Fig. 3.

The gold layer was then tested as the top pressure contact—Fig. 3. The effect was even more pronounced: the conductivity in the pressed sample is only five times inferior to that of the evaporated cell (the curves are compared in Fig. 2). Obviously, the work function of metal in the top contact under these conditions is not as essential as, e.g. the passivation of metallic surface by oxides etc. [14–18]. Notice, that under a forward bias the I/V dependence maintains the same profile under pressure, i.e., follows the Schottky expression (Table 1), while under the reverse bias the curves behave different—Fig. 3.

To prove the latter fact, both contacts were made from gold (Table 1, Fig. 3). In such a case both parts of the I/V plot were nearly symmetrical and followed the power law. Therefore, the presence of the In/PbPc interface, when In is positive, determines the exponential rise of current with the forward voltage.

On an average, 3–4 samples of each series were examined, the continuousness of the organic film before and after loading was carefully checked with an optical microscope.

¹ As we used In contacts with possible tunneling through the oxidation layer, the Fowler–Nordheim expression has also been tested [17].

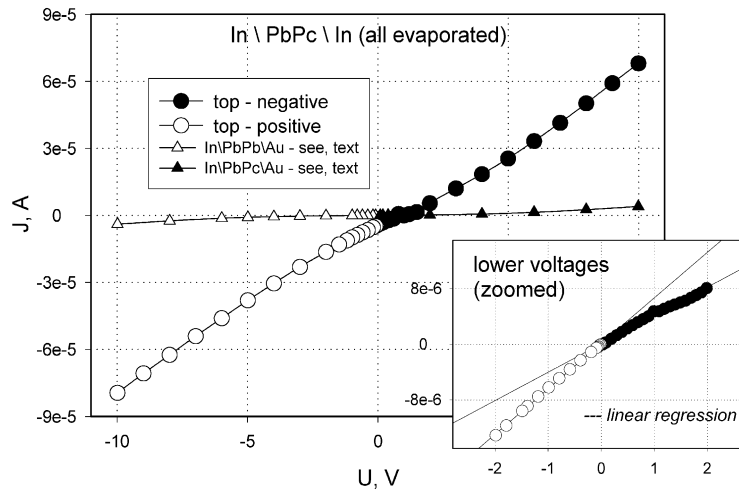


Fig. 2. Dependence of I on V for the evaporated In/PbPc/In cell (as in Fig. 1(a)) under forward (filled circles) and reverse (open circles) bias; for comparison, the forward and reverse bias curves for the In/PbPc/In (1.9 MPa pressure) cell from Fig. 3. Middle graph, are given (triangles filled and open, respectively). Inset: the low-voltage region with regression fits.

Table 1
Parameters of I/V curves shown in Figs. 2 and 3

Bias	Scheme of the cell (bottom to top)	External pressure (MPa)	Best matching dependence	Coefficient	
				a	b
Forward (top negative)	In/PbPc/In (evap.)	–	$J = aU^b$	3.8×10^{-6}	1.3
	In/PbPc/In (press.)	0 (in contact)	$J = aU^b$	0.3×10^{-9}	1.9
		0.8	$J = a(e^{bU} - 1)$	1.44×10^{-7}	0.3
		1.9	$J = a(e^{bU} - 1)$	3.46×10^{-7}	0.3
	In/PbPc/Au (press.)	0 (in contact)	$J = aU^b$	1.8×10^{-8}	1.2
		0.8	$J = a(e^{bU} - 1)$	7.3×10^{-7}	0.2
		1.9	$J = a(e^{bU} - 1)$	1.6×10^{-6}	0.2
	Au/PbPc/Au (press.)	0 (in contact)	Linear		
		0.8	$J = aU^b$	5.6×10^{-7}	1.2
		1.9	$J = aU^b$	9.5×10^{-7}	1.25
Reverse (top positive)	In/PbPc/In (evap.)	–	$J = aU^b$	5.6×10^{-6}	1.2
	In/PbPc/In (press.)	0 (in contact)	$J = aU^b$	0.5×10^{-9}	1.8
		0.8	$J = a(e^{bU} - 1)$	4.4×10^{-8}	0.35
		1.9	$J = a(e^{bU} - 1)$	2.4×10^{-7}	0.3
	In/PbPc/Au (press.)	0 (in contact)	$J = aU^b$	4.5×10^{-8}	1.1
		0.8	$J = aU^b$	4.7×10^{-7}	1.3
		1.9	$J = aU^b$	1.2×10^{-6}	1.3
	Au/PbPc/Au (press.)	0 (in contact)	Linear		
		0.8	$J = aU^b$	6.8×10^{-7}	1.3
		1.9	$J = aU^b$	1.3×10^{-6}	1.3

At least two reasons for the observed phenomenon can be hypothesized. The first one is a very likely increase in the actual contact area² for samples under pressure, which

²The surface roughness of the intact PbPc layer was greater than that of the evaporated metallic film in any case (taken with atomic force microscope, AFM SOLVER NT-MDT P7). Furthermore, if the SCLC is valid, the bulk contributions to the increase in a , such as a decrease in the effective layer thickness (or some change in the carriers mobility) under pressure, should be admitted.

results in a rise of current—Fig. 3. The second reason is changes at interfaces, which manifest themselves both in a change of the I/V profile (e.g. from power to exponential) and in the lowering of the interfacial barrier (increase in a in the Schottky expression)—Table 1. Small loads can hardly give rise to any of significant processes arising in the bulk of PbPc, for instance, a decrease in the intergrain distances in a loosely packed polycrystalline film, re-organization of crystallites or changes in the intermolecular (or interstack) packaging [7–10]. The values used are comparable with the

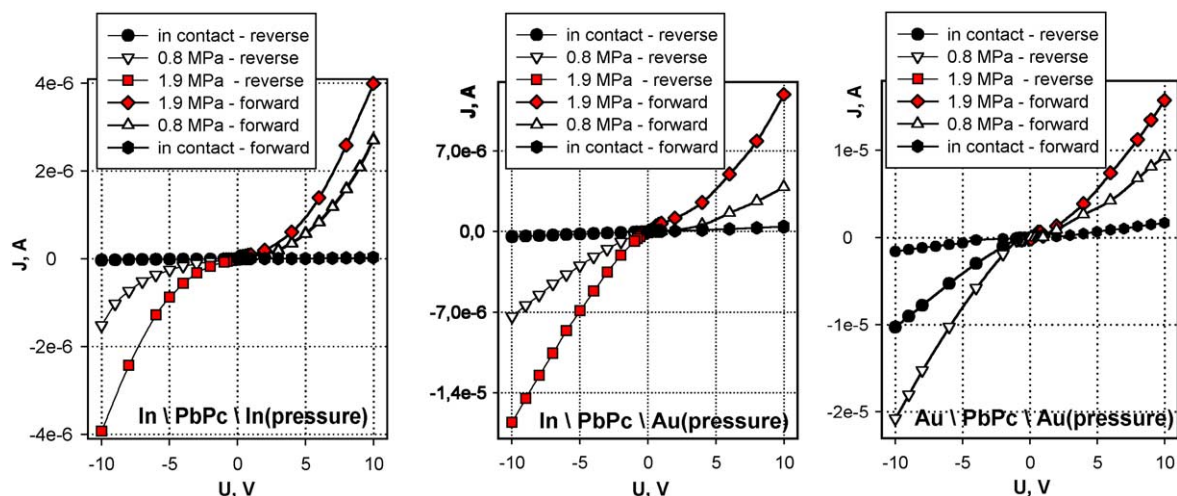


Fig. 3. Forward (hexagons, triangles up and diamonds) and reverse (circles, triangles down and squares) I/V plots for sandwich cells (as in Fig. 1(b)) with a pressure contact at zero ('in contact' state), 0.8 and 1.9 MPa. Left to right: both In contacts; bottom In contact and top Au pressure contact; both Au contacts.

pressures exerted by ordinary commercial connectors (spring clamps, crocodile clips etc.). The loaded samples exhibited a limited sensitivity to further impact—up to an order of magnitude. Higher loads were not effective due to the damage of ceramic plates. Unfortunately, the surface topology of films after use cannot be correctly estimated, as small particles of PbPc were left on the surface of the metallic pressure contact after it has been peeled off.

These results imply that the currents leaking through the conventional layered structures based on Pc's are markedly affected by the pressure or, in other words, mass of the top contact. After adding a certain, but not high, load to the cell with a simple clamping contact one can reach the overall conductivity value close to that of fully evaporated cells. Although evaporated contacts are the backbone of sandwich cells, application of a common pressure contact to relatively thick PbPc films cannot be completely disregarded, if an uniaxial pressure is applied to the cell. The individual role of the interfaces is retained in both cases. The pressure contact allows even more freedom in handling overall resistance of a heterostructure by changing the strain, with less concern for thermal [21] or current [20] damage. Further work on precise fastening of the pressure contacts to thinner films and measurements (including photo-electrical) on multi-layered heterostructures are underway.

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