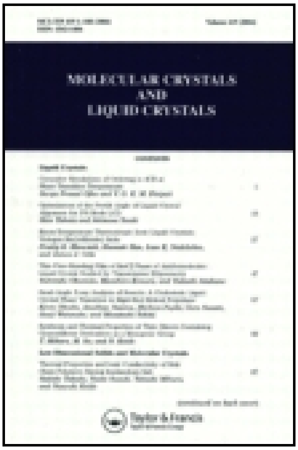

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Phthalocyanine-Based Schottky-Type Photovoltaic Cells with Magnetron Sputtered Al Electrodes

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Phthalocyanine-Based Schottky-Type Photovoltaic Cells with Magnetron Sputtered Al Electrodes

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This work addresses the use of a sputtering technique for fabricating the top contacts to conventional sandwich-type ITO\phthalocyanine\Al cells. Current-vs-voltage characteristics of these cells measured both in dark and under illumination are compared with those of identical cells, but bearing a thermally evaporated Al cathode. The greatly improved efficiency is revealed in the former case: in particular, the fill factor increased by a factor of three.

Keywords: contacts; phthalocyanines; solar cells; sputtering

1. INTRODUCTION

The problem of contacts is one of the most prominent in molecular electronics, especially in multilayer organic/inorganic devices, where the charge injection occurs through the metal/organic interface [1,2]. The overwhelming majority of such sandwich-like devices is made with thermally evaporated metallic contacts. Despite the known advantages [3], the magnetron sputtering method is very scarcely applied for the direct deposition of top contacts onto a thin molecular layer. This is likely due to the quite justified fear of damaging the underlying organic material during plasma-assisted processes [3–6]. Exceptions are known for composite electrodes, e.g., transparent conductive oxides that cannot be formed by resistive heating of components [4–8].

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Phthalocyanines (Pc) represent a large family of metallorganic compounds very widely introduced in hybrid photovoltaic and light-emitting devices [6–11]. The reason consists not only in suitable electrical and optical properties, but also in the thermal, chemical, and radiation stability highest among organic materials. The latter enables the compatibility with conventional vacuum technologies for the fabrication and the processing of inorganic devices. Earlier, the processes in thin phthalocyanine layers exposed to ion beam bombardment and plasma etching have been studied [9,10]. In this work, we report on the current-*vs*-voltage (*J*-*V*) characteristics of the prototype cells employing a photoactive Pc layer with magnetron-sputtered Al contacts. Photovoltaic properties of these cells are superior to those of cells having thermally evaporated contacts.

2. EXPERIMENTAL

Initial PcCu powder of reagent grade was purified by gradient sublimation before use. Glass slides covered with indium tin oxide, ITO layer (Aldrich, 70 Ω/cm^2) were cleaned in solvents and served further as transparent substrates. PcCu films were deposited on these substrates by a standard sublimation technique in vacuum $\sim 5 \times 10^{-5}$ Torr with a deposition rate of 0.1–0.2 nm/sec. Immediately after the deposition, the samples were transferred to the respective chambers for thermal evaporation or magnetron sputtering of metal (both made on the platform of a VUP-5M(SU) vacuum plant). Aluminum (99.99% Aldrich) was used for making top contacts. DC magnetron sputtering of a target at the 10^{-3}-Torr Ar pressure (bare vacuum $\sim 10^{-5}$ Torr) during 60 s led to the deposition of $\sim$40 nm thick metallic films on the substrate surface (at 150–200 mA discharge current). Similar thicknesses were obtained after the evaporation of pellets from W-baskets using resistive heating, through the same mask. Hereinafter, the contacts will be referred to as MS (magnetron-sputtered) or TE (thermally evaporated) contacts. The effective device area was 0.09–0.14 cm^2.

The schematic of the obtained samples is sketched in the inset to Figure 4. Experimental details and methods are described elsewhere (see, e.g., [11,12]. DC conductivity was measured under laboratory conditions in dark and under a focused illumination with a dimmed 20-W tungsten lamp installed in a two-terminal probe station. The incident light intensity was controlled by a broadband photoelectrical power meter (model IMO-4C). The *J*-*V* plots were recorded both in the steady-state and dynamic modes; and the positive potential was always on the ITO/glass substrate. The samples were placed inside a shielded grounded steel box with a small orifice for lighting. The light power delivered to the sample surface in all experiments was 6 mW/cm^2.

Additionally, the simplified sandwich structures were made for analytical studies. These consisted of metal-free phthalocyanine H_2Pc films of also 100 nm thick, sublimated under similar conditions, covered by a 20-nm-thick Al layer obtained under the same conditions by TE or MS, all deposited on the untreated surface of a silicon plate (undoped Si(100)). Such specimens contain few chemical elements in order to get non-oversaturated spectra – cf. [9]. They were studied by secondary ion mass spectrometry (SIMS) with depth profiling, using a TOF-SIMS5 installation (ION-TOF GmbH). The measurements were curried out in vacuum $<5 \times 10^{-10}$ mbar in the pulsing mode (1 ns) of a primary Bi_3 ion beam (1 pA, 25 keV). The initial spectra of structures (kept under vacuum overnight) with a mass resolution of 8–10 $\times 10^3$ M/ΔM were recorded for positive ions and analyzed in the range of 0–800 amu. Then, the depth profiles were taken with an oxygen sputtering gun (at 1 keV) in the raw data regime over the entire mass range. Profiling rates were calibrated *ex situ* from interferometry (TalySurf CCI 2000, Taylor & Hobson). The resulting crater depth was $\sim$200 nm.

3. RESULTS AND DISCUSSION

3.1. Dark and Photovoltaic Characteristics

ITO/PcCu/Al cells in dark (Figs. 1 and 2 – solid lines) demonstrate typical diode-like *J-V* characteristics reflecting the difference in the work functions of electrodes and the position of frontier molecular orbitals in PcCu [13–17] (the corresponding energetic diagram can be found, e.g., in [16]). Since we focused on photovoltaic properties here, the dark characteristics will be discussed briefly.

Similarly to [14,15], the certain hysteresis was observed at lower voltages when the sweep timing was shifted down to a millisecond range (more pronounced for the samples with TE contacts). It was accompanied by an offset of dark *J-V* curves; in addition, the current amplitude somewhat depended on the bias direction. These phenomena are attributed to recharging effects of double layer capacitance at the ITO/PcCu interface and, possibly, to ionic movement or reaction [14,15]. In our case, such by-effects vanished in the quiet regime (largely increased sweeping delay factor) or under illumination.

At the forward bias above 0.4 V, the dependences for cells with TE contacts consisted of two sections in semilogarithmic coordinates,

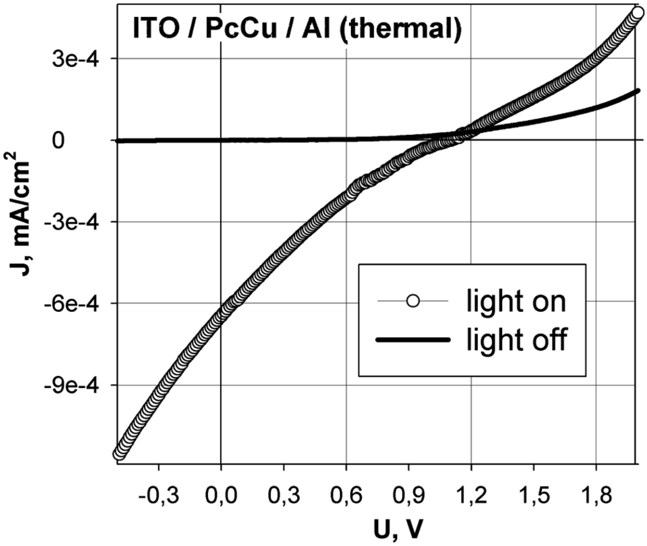

FIGURE 1 *J-V* curves measured in dark and under illumination for ITO/PcCu/Al cells with TE top contacts.

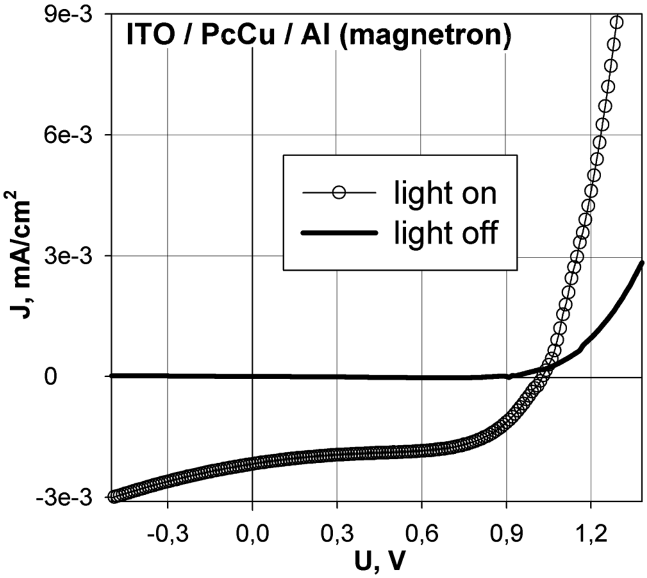

FIGURE 2 *J-V* curves measured in dark and under illumination for ITO/PcCu/Al cells with MS top contacts.

which is typical of metal/Pc/metal structures comprising both electrode-limited and bulk-limited conduction mechanisms [13,16–18]. For the cells with ME contacts, the dependences were even more complex, so that only the high-voltage section ($>1.5\,\mathrm{V}$) can be linearized on the log-log scale (i.e., they obey the power law with the exponent similar to 5.3).

Though the nominal thickness of the PcCu layer remains the same, dark current densities in the cells with MS contacts were greater by about 1.5 orders of magnitude (at 1.2 V, positive bias) – Figures 1 and 2. The rectifying behavior of the cells rose up, too.

The distinctions become more interesting and clear, when ITO/PcCu/Al cells are exposed to illumination (Figs. 1 and 2 – lines with circles). Quantitative parameters are summarized in Table 1 (here, V_{max} and J_{max} are the voltage and current density corresponding to the maximum power point of the cell; other parameters are interpreted in the text below). As immediately seen from Figures 1 and 2, the "squareness" of the J-V plot of samples with MS contacts in the third quadrant is markedly better. The corresponding fill factor (FF) is 3 times greater than that derived for TE contacts (see Table 1). Furthermore, the light-assisted currents leaking through the cells with MS contacts are 2 orders of magnitude greater. One of the reasons should be associated with the partial elimination of parasitic resistances: namely, the series resistance R_{s} strongly decreases (Table 1), whilst the shunt resistance increases slightly ($R_{\mathrm{sh}} \approx 1.3\text{–}1.5 \times 10^3\ \mathrm{k\Omega\,cm^2}$). Short-circuit current J_{sc} increases, as well as the relative photoresponse of the current at a constant bias. Since the photon-absorbing/transporting material (PcCu) is the same, this points to the increased efficiency of charge carrier collection at the Al electrode [18].

All these factors lead to the improvement of the power conversion efficiency η by about one order of magnitude. Note that the open circuit voltage V_{oc} is almost unaffected by the deposition method (Table 1). Indeed, one can expect the retained mismatch between the corresponding energy levels, since the interfaced materials pair (PcCu + Al)

TABLE 1 Parameters of ITO/PcCu/Al cells derived from J-V characteristics shown in Figures 1 and 2

Parameter	V_{oc} (V)	J_{sc} (mA/cm^2)	V_{max} (V)	J_{max} (mA/cm^2)	FF	R_{s} (kΩ cm^2)	η (%)
PcCu/Al-TE	1.10	6.4×10^{-4}	0.45	3.1×10^{-4}	0.19	3.4×10^3	0.0022
PcCu/Al-MS	1.02	2.2×10^{-3}	0.76	1.7×10^{-3}	0.57	98	0.021

remains virtually unchanged. This also means that no interlayer (e.g., a highly carbonized region that would appear during the sputtering process) is inserted at the Al/Pc interface.

Moderate annealing slightly modifies the shape of curves: the photoresponse deteriorates for both TE and MS contacts (the latter is more stable), but arouse no substantial degradation or breakdown in the samples.

Therefore, judging from the electrical testing only, the explanation of the observed differences would consist in the adhesion improvement of the Al layer during the magnetron sputtering process due to (a) sputter cleaning of weakly bonded impurities on the PcCu surface and (b) better mechanical mixing with more energetic atoms [3]. This simply implies a "better" contact. The morphology and, hence, R_s of the thin Al overlayer itself are also different, as seen from the microscopic images (not shown here). However, the evolution of the deposition surface, owing to e.g., chemical reactions, and the appearance of chemically active sites, new species, etc., cannot be ruled out. We thus proceed to an analytical method which is required to monitor this evolution in more details.

3.2. Analysis of the interfaces

In the next stage of the work, the actual situation at the metal/phthalocyanine interface was investigated by SIMS profiling. First of all, our result shows that the penetration (diffusion, shallow pre-implantation) of metal atoms into the film depth in the case of MS contacts is quite not so intensive, perhaps even weaker than that in sandwiches with TE contacts. This is illustrated in Figure 3 (see also inset in Figure 4 for clarity), where the depth profiles of basic elements composing the top layer (Al), organic film (carbon), and substrate (silicon) are given. It is not unlikely, that reactive Al atoms (in contrast to, e.g., noble metals such as Au) interact with molecules on the surface [2], by thus preventing the further migration and the formation of a diffuse junction. The fact that MS contacts may form a stable abrupt interface is important, since other researchers describe mostly radiation-induced damages, which is unwanted and must be minimized in any case [4–6].

Furthermore, the complex ions (clusters) that may be considered as products of the reaction of Al with a Pc molecule were carefully checked throughout the raw data on both interfaces (more than 40 possible combinations have been traced). For instance, the interaction of condensing metal atoms with the C…N…C macroring of a phthalocyanine molecule on the surface is thought to give rise to the

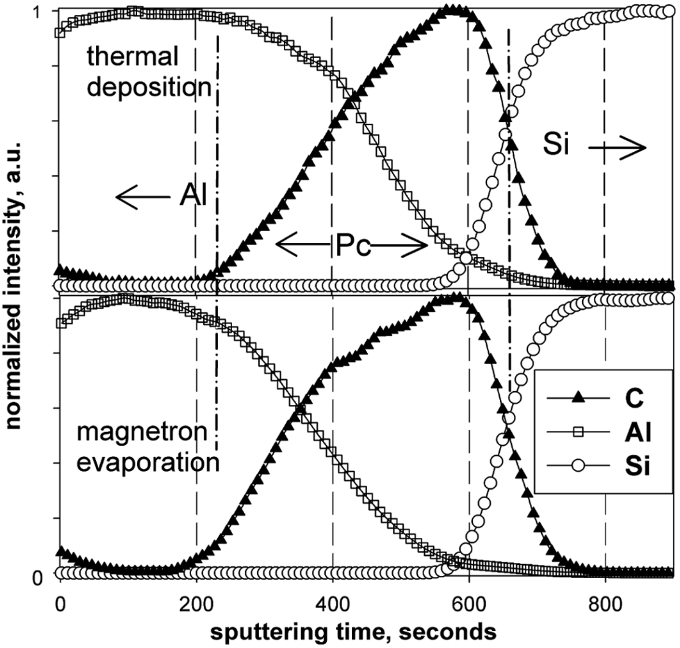

FIGURE 3 SIMS profiling (from left to right) of Al, C, and Si ions in the Al/H_2Pc/Si heterostructure with TE (top) and MS (bottom) thin Al layers. Bulk materials are depicted with gray arrows; and the approximate location of interfaces is marked by dash-dotted gray lines.

formation of Al-C or Al-N bonds. It can, in turn, be concluded from an increased yield of Al-C- or Al-N-containing species in SIMS spectra. The latter is undoubtedly confirmed by the data presented in Figure 4. As seen from the SIMS profiles given in this figure, the relative concentration of characteristic C-Al-C and C-Al-N ions in the vicinity of the Al/Pc interface (reached after ~320–380 s of sputtering) is higher for the Pc films with MS contacts.*

Meanwhile, it is known that the formation of Al-C covalent bonds can be responsible for a modification of the bonding pattern of conjugated macromolecules [19] or the stoichiometry of interfacial adducts [20] and hence plays a crucial role in the electronic transport from the top metal to the underlying organic film [2,19,20]. The facilitated

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*Note that the y-axes are given in normalized intensities. Deliberately, the profiles of various ions in the Pc film depth and in the vicinity of the second interface, i.e., Pc/substrate (reached after ~600–620 s of sputtering – see, Figures 3 and 4), as well as possible oxidative processes, are not discussed here. Those data will be published elsewhere.

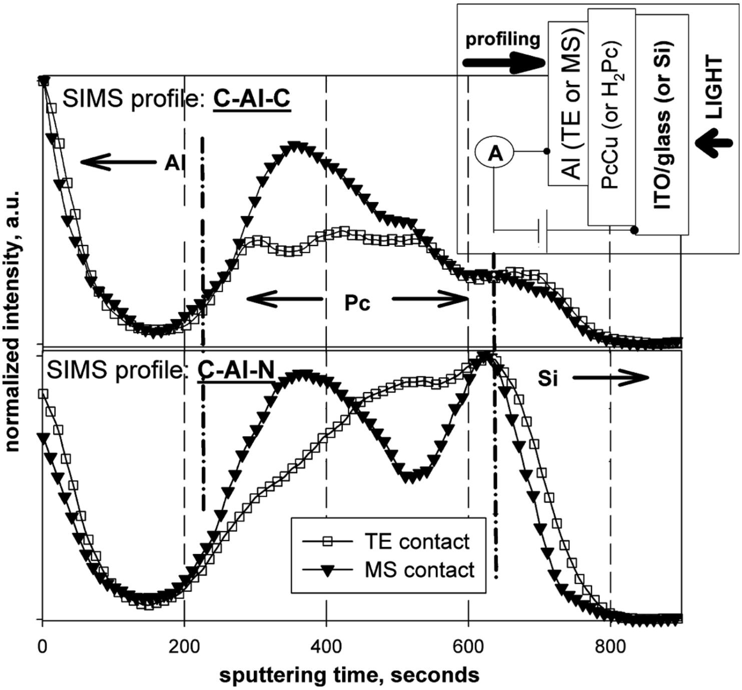

FIGURE 4 SIMS profiles for AlC_2 (top) and AlCN (bottom) ions in the Al/H_2 Pc/Si heterostructure (same as in Fig. 3). Inset: schematic of samples.

charge injection from bottommost metallic atoms into the electronic system of adjacent molecules may be hypothesized in the case of MS contacts. Thereby, the prevailing chemical reconstruction of the Metal/Pc interface in the case of an MS aluminum layer has to be included in the list of mechanisms explaining the observed improvement of the photovoltaic parameters of cells.

4. CONCLUSION

The parameters of the Schottky-type photovoltaic cells have been substantially improved by using the magnetron sputtering technique for the fabrication of an Al cathode. Devices with MS contacts demonstrate a stronger rectification, lower resistivities, and greatly increased efficiency, as compared to their counterparts with thermally evaporated contacts. The analytical investigation (SIMS) suggests that these effects can be attributed to the enhanced surface reactions with metal atoms during the sputtering process, which finally results in the formation of a more effective contact to the molecular film.

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