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Rectification and NIR photoresponse in p-Si/phthalocyanine/metal heterostructures

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Abstract

Hybrid organic-on-inorganic heterostructures employing phthalocyanine molecular semiconductor and doped silicon were fabricated using standard microelectronic processes. Current-vs-voltage characteristics display rectifying behavior of such heterostructures, which becomes more pronounced if n-type phthalocyanine layer is utilized. Competitive influence of phthalocyanine/metal and phthalocyanine/p-Si interface on electrical transport in the devices is discussed. Heterostructures with lead phthalocyanine layer show photoconductive properties in the NIR domain when illuminated through p-Si side.

Keywords: Heterostructures; Phthalocyanines; Photoconductivity

1. Introduction

The hybrid heterostructures incorporating both organic (molecular) and inorganic (silicon, gallium arsenide, II–V group, oxides) semiconductors gain increasing interest due to their prospective application in photovoltaic devices. Phthalocyanines are very promising candidates for application in such heterostructures, since unique thermal and chemical stability makes them fully compatible with conventional semiconductor technologies and processing [1–5]. Instances of organic-on-inorganic structures based on the p-Si/ or n-Si/phthalocyanine heterojunctions can be found in Refs. [2,6–12] or [3,12–21], respectively.

On the other hand, several transition metal phthalocyanines (PcMet) exhibit weak absorption bands in the near infrared ($>1\,\mu m$) due to singlet–triplet (PcCu, PcPb [22]) or singlet electronic transitions (double-decker compounds [23]) in the molecule. This in turn leads to appearance of the photoconductivity in thin films or crystals at corresponding wavelengths, that is well beyond commonly reported photosensitivity range of the phthalocyanine-based devices (0.6–0.9 μm) [1–3,6,7,9–11,14,15,17–19,21]. Therefore, it is not unlikely that, for instance, heavily doped silicon may be utilized as a transparent contact for measurements of photo-generated currents in the NIR or even mid IR domain [22,23] instead of routinely used indium–tin oxide (ITO), which has limited transmission above ~2–2.5 μm.

In the present work, the steady-state current vs voltage (I/V) characteristics of sandwich-type heterostructures, denoted as p-Si/PcMet/metal in the following, are examined with particular interest in their rectifying properties. Photoresponse in the near infrared was also detected.

2. Experimental

At first, the Al/p-Si/Ta_2O_5 substrates have been fabricated (inset in Fig. 1). A 0.6 μm thick Ta_2O_5 dielectric layer was deposited by magnetron sputtering through the mask on the B-doped Si(1 0 0) wafers ($\rho = 10\,\Omega\,cm$), in which backohmic contacts were formed by evaporation and sintering of Al. After removal of the mask, a window (diameter of $1\,mm^2$) remained in the middle of Ta_2O_5 dielectric layer.

Immediately after etching and washing (25%HF:H_2O and DI water, respectively) of the surface of silicon wafer in this window, the substrates were placed in a VUP-5 vacuum station (~10^{-3} Pa). Lead phthalocyanine (PcPb)

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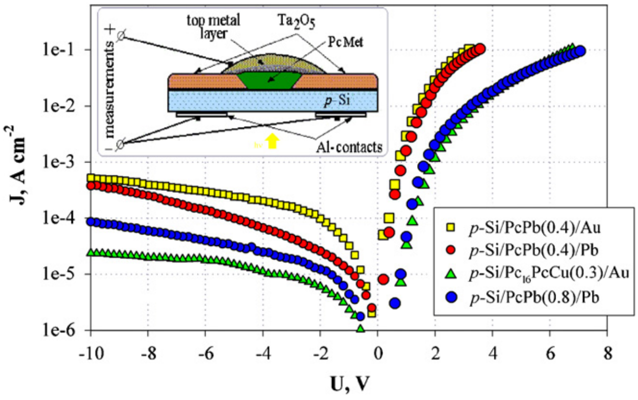

Fig. 1. *I*/*V* plots (semi-log scale) for the heterostructures with various PcMet layers (thickness in μm is given in parentheses) measured under laboratory conditions, room temperature. Schematic of the samples (cross-sectional view) is shown in the inset.

or copper hexadecachlorophthalocyanine ($Cl_{16}PcCu$) films were deposited in the window area using a standard vacuum sublimation technique through the shadow mask. Then, the top metal layer (i.e., second electrode) of somewhat larger diameter was evaporated—Fig. 1, inset. The evaporation rate of PcMet (0.1–0.2 nm/s) was monitored by a quartz crystal microbalance with subsequent verification of thickness by interference microscopy. The substrate temperature did not exceed 40 °C. Finally, the high density Ta capping layer was sputtered for mounting the clamp contact, so that the overall metallization height was ~0.8 μm. The samples thus obtained were further used for (photo-) electrical measurements in the laboratory conditions (Supplementary info).

The PcMet films on pre-treated Si-substrates were characterized by optical spectroscopy, atomic force microscopy and X-ray diffraction. In particular, the continuousness and morphology of the films were carefully examined in order inspect and avoid possible pinholes or channels [6,21] (Supplementary info). Details of (photo-) electrical measurements are described earlier [23,24].

3. Results and discussion

All the heterostructures in this study showed rectifying behavior, with the forward bias corresponding to positively charged Al/p-Si contact—Fig. 1. The rectifying ratio at 1 V was ~10^2 (that is comparable with previously reported values-Supplementary info). As immediately seen from the Figs. 1,2, profiles of *I*/*V* plots and conductivity values depend on the type of the molecules composing the organic layer. This was also proved by measuring the reference samples, in which the top metal contact of the same active area was deposited directly on p-Si [21,25] or Ta_2O_5 (see, e.g. Fig. 2[1]).

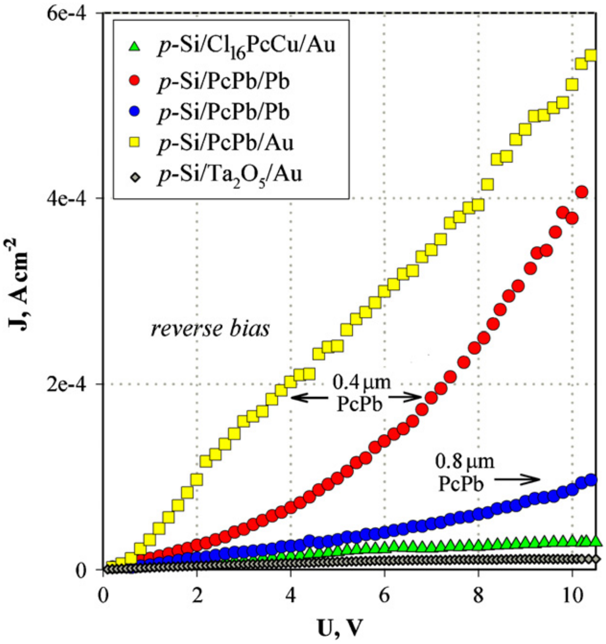

Fig. 2. Reverse bias *I*/*V* plots (linear scale) for the same heterostructures as shown in Fig. 1. For comparison, the *I*/*V* plot of the reference sample with blank dielectric is given.

All experimental curves under the forward bias can be linearized in log–log coordinates ($R > 0.99$). In the corresponding equation $J = \text{const} * U^m$, the power coefficient m is equal to 2.5–2.8 for PcPb and to 3.5 for $Cl_{16}PcCu$-based heterostructures, respectively (except few points at $U < 1$ V). This formally implies transition to the space charge limited currents (SCLC) with exponential distribution of traps [26]. Although thermionic emission mechanism is usually proposed [6,7,10,11] for modeling the forward bias characteristics in p-Si/p-PcMet junctions, SCLC regimes can also be observed [6,7], typically at higher voltages (>1 V). (Besides, SCLC have been evidenced in [25] for n-Si/n-PTCDA($C_{24}O_6H_8$) junction).

In Fig. 2, the reverse bias *I*/*V* plots are shown in detail. Generally speaking, there are two interfaces affecting the transport across these heterostructures: p-Si substrate/PcMet and PcMet/top metal [6]. As known, Au provides ohmic contact to both PcMet [24,26–28]. Metals with a lower work function, such as Pb, are expected to give rectifying contacts with p-type PcMet [26,28]. Indeed, the *I*/*V* plot is linear in the case of Au top contact—Fig. 2.

Using Pb as top contact to p-PcPb instead of Au leads to nonlinear I/V plots under the reverse bias—Fig. 2. No "soft breakdown" was found in the studied voltage range [11,25]. Experimental data are best approximated by equation

$$J = AT^2 \exp(-\Phi_o/kT) \exp(\beta_s U^{1/2}/kTd^{1/2}),$$

where A is a Richardson constant, Φ_o, barrier height, $\beta_s = (\varepsilon^3/4\pi\varepsilon_\tau\varepsilon_o)^{1/2}$, theoretical Schottky coefficient, and d, distance [25,26]. This mechanism frequently manifests itself

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[1] Although Ta_2O_5 is shown to be a high quality dielectric material [30], it was necessary to verify whether it acts as parasitic parallel resistance in our scheme or not.