Photovoltaic Behaviour of Titanyl Phthalocyanine Thin Films and Titania Bilayer Films

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Summary: Titanyl phthalocyanine (TiOPc) thin films were prepared using evaporation and surface polymerization by ion-assisted deposition (SPIAD) in a vacuum deposition system. These films were characterized by means of ultraviolet and X-ray photoelectron spectroscopy as well as UV/Vis absorption spectroscopy. Valence band and elemental content indicated that phthalocyanine electronic and chemical structures were largely preserved during SPIAD. Further, bilayer thin films of titania (TiO_2) and SPIAD TiOPc were prepared. TiO_2 film was deposited by reactive magnetron sputtering of TiO_2 target. Study of the structured samples was focused on the optical and electrical properties of the composite films. The films were characterized by non-contact photovoltage measurements and UV-Vis spectroscopy. These results suggest there is a possibility to use these bilayer thin films in photovoltaic solar cells, however further experiments to improve conductivity of the films will be required.

Keywords: conjugated polymers; photovoltaics; phthalocyanine; thin films; titania

Introduction

Organic materials are being extensively studied because of numerous advantageous properties with many areas of possible application. One class of these organics is phthalocyanines (abbreviated Pc). They are highly stable, economical and easy to handle. Phthalocyanine films have been studied for their possible use in solar cells, field effect transistors and organic light emitting devices (OLEDs). Their structure is highly conjugated with a polyaromatic ring that can be bound to a divalent transition metal (MPc) or to hydrogen (H_2Pc). The nature of the central metal atom partly affects photophysical properties of the phthalocyanines and is closely related to the charge or the behavior of the photogenerated charge. With an absorbance spectrum that matches the solar spectrum, phthalocyanines are good candidates for e^- donor in organic solar cells. Thin films of these materials can be prepared by various techniques, either wet (doctor blading, spin coating, etc.) or evaporation in vacuum. Another possibility is via surface polymerization by ion-assisted deposition (SPIAD) which has been previously demonstrated as an effective method for the production of thin films of polythiophene and polyphenylene by the simultaneous deposition of polyatomic ions and evaporated neutrals.[1–3] These studies showed unique optical properties compared to the evaporated monomeric films by varying the ion to neutral ratios. These results also suggested that SPIAD can be used for polymerization of various types of compounds, especially organic compounds with extended π-bonding networks. We focus in this paper on studying the electrical and photovoltaic properties of evaporated and SPIAD titanyl phthalocyanine films.

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To utilize the suitable properties of phthalocyanine thin films in solar cells, it is convenient to create a donor-acceptor interface where the charge separation occurs.[4] One possible solution is formation of a heterojunction device. It can either be a bilayer heterojunction, a bulk heterojunction or a diffuse bilayer heterojunction. One of the most widely utilised and studied semiconductor materials is titania (TiO_2). Titania is n-type material and its film is proposed to serve as an electron transporting layer. This study describes properties of titanyl phthalocyanine films without and with a deposited titania layer.

Experimental Part

Deposition of titanyl phthalocyanine (TiOPc) films for the purpose of this study was carried out in an UHV apparatus by simple evaporation in vacuum (325–340 °C) and surface polymerization by ion-assisted deposition (SPIAD) (Figure 1a). SPIAD films were produced via simultaneous deposition of neutral TiOPc with 50 eV polyatomic acetylene ions ($C_2H_x^+$, $x = 0,1,2$) at ion current of 1.3 $\mu A/cm^2$ at 45° incident angle and at 1/1 ion to neutral ratio.[5] An organic doser was employed for thermal evaporation of neutral TiOPc.

The vacuum deposition apparatus (see Figure 1b) for titania thin film preparation by DC magnetron sputtering consisted of a balanced planar magnetron (M in Figure 1b) placed under a substrate holder (S) attached to the chamber via a load-lock system (L) at a distance of 40 mm. The films were prepared by a reactive method using a mixture of argon and oxygen as a working gas (17% of O_2) admitted into the apparatus through a needle valve. Working gas pressure and its total flow rate were held constant at 5 Pa and 6 cm^3_{STP}/min, respectively. The magnetron with TiO_2 target was powered from an Advanced Energy 1.5 DC power supply. The DC power supply was operated in a ‘constant current’ mode at 0.2 A, which corresponds to 100 W power. Details of the deposition methods and analysis techniques can be found elsewhere.[1–3,5,6]

UV-Vis transmittance and reflectance spectra were measured using a commercial spectrometer Perkin Elmer Lambda 35 and

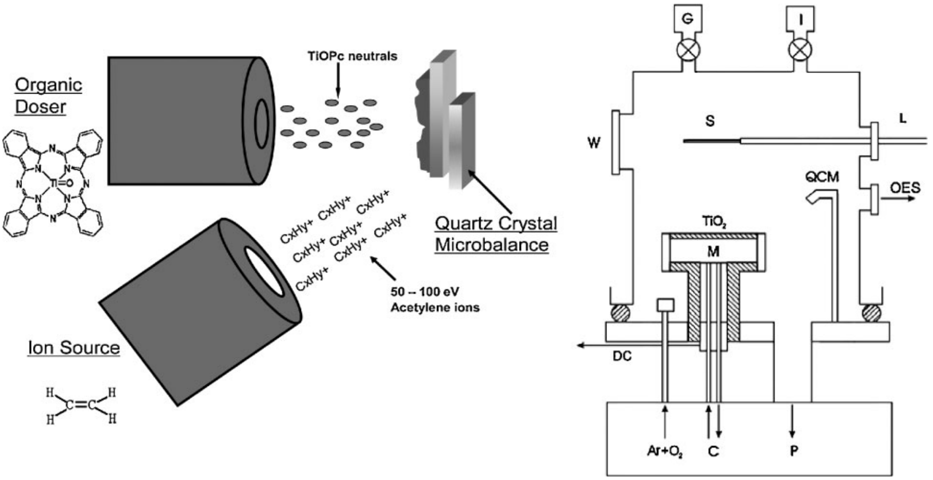

Figure 1.

a) Schematic of the SPIAD method; b) Diagram of the vacuum deposition apparatus. $Ar+O_2$ – inlet of working gas (argon and oxygen mixture), C – magnetron water cooling, DC – to DC power source, G – baratron, I – ionization gauge, L – load-lock, M – magnetron, OES – to optical emission spectrometer, P – to rotary and diffusion pumps, QCM – quartz crystal microbalance, S – substrate holder, TiO_2 – titanium dioxide target, W – window.

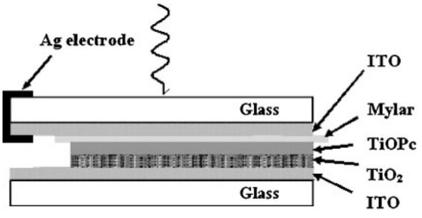

Figure 2.
Structure of a TiO_2/TiOPc sample for SPV measurement.

integration sphere Labsphere RSA-PE-20 with USRS-99-010 standard. The samples for optical measurements were prepared on fused silica substrates. Layer thicknesses were measured using a KLA-Tencor P-10 profilometer. Surface photovoltage spectra were measured on an automatic apparatus keeping the impinging photon flux density constant. In order to measure the SPV spectra, the sample prepared on glass with ITO was covered by thin Mylar film and another glass with ITO was placed on top of it which formed a sandwich, as can be seen in Figure 2. Samples were illuminated from the side of the TiOPc absorber, through the additional ITO and Mylar.

Results and Discussion

The UV-vis absorption spectra of SPIAD and evaporated samples are displayed in Figure 3. The lowest-energy absorption band with maxima located at 726 and 729 nm in SPIAD and evaporated samples, respectively, corresponded to the characteristic Q-band assigned to π–π^* transition of conjugated systems. SPIAD samples had a higher absorption coefficient than the evaporated ones. The optical energy band gap (E_g) of polymers was evaluated from the thin film absorption edge and it was nearly the same for the both SPIAD and evaporated films - 1.55 and 1.54 eV, respectively.

These values are in good agreement with the results obtained by ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS, respectively).[5] It can be seen that the shapes of UV-vis spectra for SPIAD and evaporated samples are very similar to each other. This corresponds to the similarity of UP and XP spectra of the films. UPS and XPS also showed at least some covalent bonding between adjacent TiOPc molecules to form dimers during SPIAD that did not occur by evaporation. These results indicated that phthalocyanine electronic and chemical structures were largely preserved during SPIAD. The SPIAD samples' higher absorption may have been due to bonding.

The surface photovoltage (SPV) spectra of SPIAD deposited and evaporated TiOPc thin films are shown in Figure 4. The photovoltage depended on the wavelength of the illuminating light for both SPIAD deposited and evaporated films. It can be seen that the SPV spectra for SPIAD deposited and evaporated TiOPc are

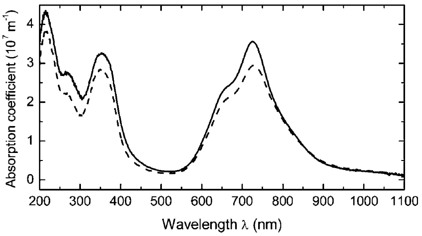

Figure 3.
UV-vis absorption spectra of SPIAD (solid) and evaporated (dashed) samples.

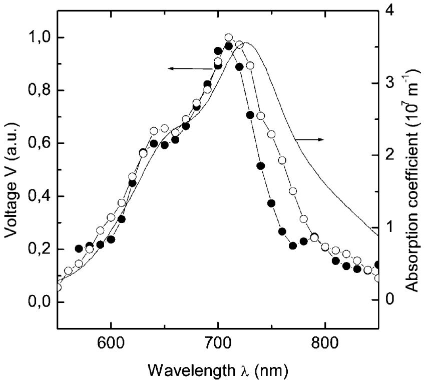

Figure 4.
Normalized SPV spectra of a) 15-nm SPIAD (solid circles) and 30-nm evaporated (open circles) films compared with the SPIAD film absorption

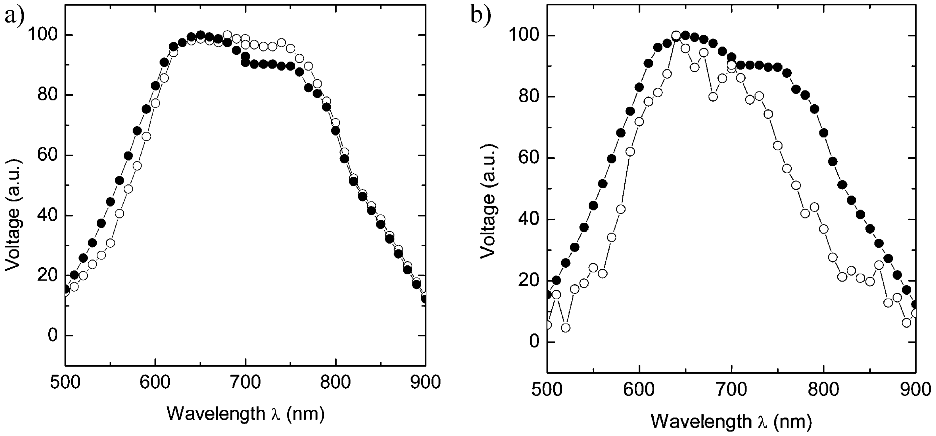

Figure 5.
Normalized SPV spectra of a) TiO_2/TiOPc films: SPIAD deposited (solid circles) and evaporated (open circles) and b) SPIAD deposited TiO_2/TiOPc bilayer (solid circles) and single layer (open circles) samples. TiOPc thickness: SPIAD deposited was 220 nm and evaporated 250 nm.

similar to each other and clearly correlate with the UV-vis absorption spectra.

The photovoltage spectra of bilayer films TiO_2/TiOPc are shown in Figure 5a. The spectra for SPIAD deposited and evaporated films are also similar to each other, but they are much broader than those displayed in Figure 4.

The difference could be assigned to the different thicknesses of the TiOPc layer as is illustrated in Figure 5b, where the SPV spectrum of 220-nm SPIAD deposited TiOPc layer is shown. Future work will use SPV theory[7] to analyze the experimental data. The surface photovoltage in a thin layer is a result of dissociation of photogenerated free excitons in electric field of the space charge region which forms spontaneously at the surface. Fitting SPV theory to the experimental data, the thickness of the space charge region and the diffusion lengths can be evaluated.

Conclusions

In conclusion, the data presented here does not shown any large differences between the surface photovoltage measurements of SPIAD vs. evaporated titanyl phthalocyanine films. Phthalocyanine electronic and chemical structure was largely preserved during SPIAD and the dimerization of TiOPc observed previously did not appear to affect the photoresponse. Photoresponse of the material shown in the photovoltage spectra matched well the solar spectrum, which suggests a possibility to use these bilayer thin films in photovoltaic solar cells.

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