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Vacuum co-deposition of organic solar cell structures

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An algorithm for calculation the mass ratio between evaporated components in vacuum co-deposition is presented. The algorithm is demonstrated via preparation of organic solar cells. Zinc phthalocyanine (ZnPc) based solar cell samples of types ITO|PEDOT:PSS|ZnPc:C_{60}|Al were prepared in a clean room conditions. The active bulk heterojunction (BHJ) organic composite ZnPc:C_{60} film was prepared with mass ratio of 4.2:1. The surface morphology was characterized by SEM. Photoelectrical measurements were carried out on the samples prepared, demonstrating the advantages of the composite material with respect to the single ZnPc layer. The algorithm developed allows further precise optimization of the BHJ cells to be performed.

Keywords: vacuum co-deposition, organic electronics, solar cells.

INTRODUCTION

Thin films of low molecular weight semiconductors are usually prepared by variety of complex techniques, including physical or chemical vapour deposition, organic molecular beam epitaxy or solution-based deposition techniques. The performance of small molecular organic devices is highly sensitive to the film morphology and processing conditions. Often, the solution-deposited active layers of devices (e.g. spin coated films) exhibit a high portion of microcrystallites and aggregates. The vapour deposition techniques provide high-quality crystalline films characterized by improved charge-transport properties compared with those of solution-deposited films. The vacuum technique has the advantage of dry film deposition process excluding the usage of solvents. Moreover this technique provides more opportunities to control important film parameters as film thickness and uniformity. As a consequence the films deposited exhibit more stable and reproducible properties with a comparison to solution deposited films.

In the last decades it has been shown that the charge separation on the donor acceptor interface considerable increases the efficiency [1].

The simplest way to provide the charge separation in the organic substances is the formation of bi-layer donor/acceptor structure [2]. In case of insoluble donor and acceptor materials the vacuum deposition suggests possible solution for bi-layer structure formation.

Further increase of the efficiency was achieved introducing p-i-n structures. Pfeiffer and co-workers [3, 4] have developed p-i-n technology using high vacuum deposition process. Efficiency of 3.6% has been obtained.

The exciton diffusion length in the organic semiconductors is about 10 nm but the optimized light absorption requires film thicknesses of about 100 nm. This discrepancy makes the bi-layer structure less effective.

This problem is overcome later developing the BHJ structure. BHJ comprises an active layer with mixed donor and acceptor species to allow for much thicker films to better absorb sunlight [5]. Vacuum co-deposition allows easier way to obtain BHJ composite layer, grown from insoluble

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components.

Also the optimization of the organic solar cells needs a variety of additional layers to be deposited like hole transporting layer (HTL), electron transporting layer (ETL), electron blocking layer (EBL), etc. Such a comprehensive multilayer structure is usually obtained by subsequent vacuum deposition of separate layers without breaking the vacuum.

Following the strategy of the multilayer devices a tandem solar cell was developed [6, 7]

The ultimate goal of stacking PHJ solar cells in a tandem configuration is to have many interfaces for efficient exciton dissociation while maintaining a summative thick film for absorption of light. One may also absorbs a broader spectrum of light through the use of different donor/acceptor materials with different absorption characteristics. [2]. Producing multilayer structure by ‘wet’ process technology is not reproducible. The deposition of the subsequent layers should not dissolve the sublayers. This problem is successfully overcome by vacuum technology giving in this way the open field for the multilayer and tandem type devices. In all these cases the vacuum preparation of BHJ suffers from precise control of the components, which is maintained by controlling the deposition rates.

This work aimed to develop an algorithm for *in situ* determination of the mass ratio between components in BHJ composite based solar cells during the vacuum co-deposition process.

EXPERIMENTAL

Calculation of the deposition parameters

The co-deposition process is controlled by two channels Quartz Crystal Microbalance (QCM) where the *in situ* thickness measurement is based on Sauerbrey’s equation [8]. To keep a correct ratio between the evaporated components a precise determination of the film densities (D_A, D_B), tooling (U_A, U_B) have to be done according to the QCM manual [9].

The calculation assumes two QCM sensors for independent measurements of the deposition rate as depicted on Fig 1. After correct setting of the aforementioned parameters for both materials and a choice of desired mass ratio ($M^H_{A/B}$) and total film thickness (T^H_{AB}) the following relations could be derived:

$$M^H_{A/B} = \frac{U_A}{U_B} M^S_{A/B} \qquad (1)$$

$$M^S_{A/B} = \frac{M^S_A}{M^S_B} \qquad (2)$$

$$M^S_A = D_A T^S_A \qquad M^S_B = D_B T^S_B \qquad (3, 4)$$

$$T^H_A = U_A T^S_A \qquad T^H_B = U_B T^S_B \qquad (5, 6)$$

$$T^H_{AB} = T^H_A + T^H_B \qquad (7)$$

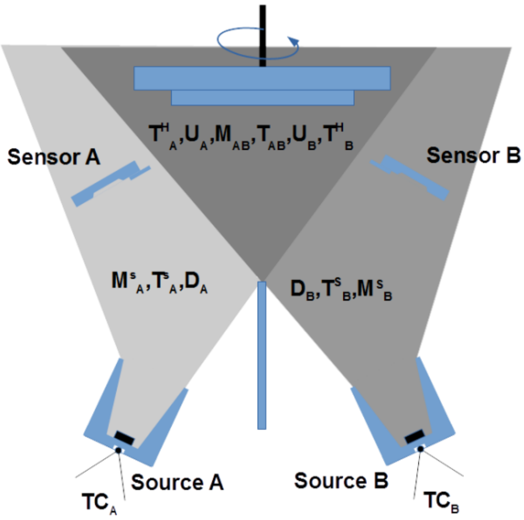


Fig. 1. Schematic draw of the co-deposition process. The parameters, denoted on the scheme are explained in the equations.

Solving this set of equations the unknown parameters, namely the mass ratio of materials *A* and *B*, which could be obtained at the sensors ($M^S_{A/B}$), mass of material *A* at the sensor *A* (M^S_A), mass of material *B* at the sensor *B* (M^S_B), thicknesses of films (T^S_A, T^S_B), deposited at sensor *A* and *B*, respectively, and the thicknesses of films (T^H_A, T^H_B), deposited on the holder during a separate deposition of material *A* or *B*, respectively, are determined. The parameters T^H_A and T^H_B are more essential as they appear as thickness reading on the QCM display after finishing the co-deposition process.

By the choice of a proper rate of deposition for material *A*, at the position of the holder (R^H_A), the time of the deposition *t* and the corresponding deposition rate for material *B* at the position of the holder (R^H_B) could be calculated by equations:

$$t = {T^H_A}\big/{R^H_A} \qquad R^H_B = {T^H_B}\big/{t} \qquad (8, 9)$$

After setting of R^H_A and R^H_B as a given rates for the QCM PID regulators the co-deposition process could start. It is useful to calculate the rate ratio $R^H_{A/B} = {R^H_A}\big/{R^H_B}$ and plot it as a function of *t* during the deposition process. As the PID controlled R^H_A

and R_B^H always oscillate the $R_{A/B}^H$ parameter could be used to introduce *in situ* corrections. A computer software for co-deposition process control was developed by the authors

Methods

The samples for photoelectrical measurement (patterned ITO Ossila substrates) were preliminary cleaned. On some of the substrates PEDOT:PSS film was deposited by spin coating at 5500 rpm for 60 seconds. Subsequent annealing for 10 minutes at 150°C on air and 10 minutes at 150°C in nitrogen atmosphere was applied to remove the residual moisture.

The organic composite and electrode films were prepared in a clean room class C (M. Braun Inertgas-Systeme GmbH, Garching, Germany). ZnPc:C_{60} composite thin films were deposited by co-evaporation of ZnPc and C_{60} onto Ossila substrates through a proper deposition mask. The deposition was performed in a vacuum system from two thermally heated sources at evaporation temperatures of about 500 and 430ºC, respectively.

The calculations based on the aforementioned set of equations show that for a given composite ZnPc:C_{60} film with thickness of 130 nm and a mass ratio of 4.2 the ratio between the evaporated rates of the two components have to be set at 3.3. These calculations are based on the experimentally obtained for ZnPc and C_{60} densities of 1.25 and 1.36 g/cm^3, respectively, and tooling factors of 0.29 and 0.21, respectively. Assuming ZnPc deposition rate of 5 Å/s, the C_{60} rate of 1.5 Å/s was obtained. These calculations demonstrate the importance of the algorithm developed. ZnPc and C_{60} deposition rates were controlled by two independent channels of quartz crystal microbalance (Inficon SQC 310C).

The solar cell samples of type ITO|PEDOT:PSS|ZnPc:C_{60}|Al were measured in nitrogen atmosphere. For comparison I-V characteristics of ITO|ZnPc|Al sample with single ZnPc layer were also determined. During the measurement the samples were exposed to a light according to the standard AM 1.5, produced by solar simulator LS0916 LOT Oriel class AAA. The light intensity of about 830 mW.cm^{-2} was controlled by a calibrated reference silicon cell RR200O (ReRa Solutions BV; Nijmegen, Netherlands). The current voltage (*IV*) characteristics were measured by Keithley 6487 electrometer (Keithley Instruments Inc., Cleveland, OH, U.S.A.).

The morphology of the films was investigated by scanning electron microscope (SEM) Philips 515 at accelerating voltage of 25 kV. The samples for SEM characterization were deposited on microscopic glasses. Before the SEM study the sample surface was covered consecutively by carbon and palladium/gold films.

Thickness of the layers was measured by Decktak XT profilometer.

RESULTS AND DISCUSSION

Film deposition

Fig. 2 presents typical rates in a co-deposition process for a preparation of ZnPc:C_{60} composite as an active BHJ layer with organic solar cell application. Right ordinate presents the rate R_{ZnPc}/R_{C60} ratio, calculated during the deposition process. The calculation of the rate ratio is useful for *in situ* corrections of the PID parameters to achieve more precise co-deposition control. It could be seen that the ratio between the evaporated rates is more sensitive towards the deviation of the given parameters than the evaporated rates themselves. Presented in the figure mean values of the rates and their standard deviations are calculated after finishing of the deposition process. It is seen from the figure that a precise automatic control of the rates with a standard deviation of ±0.1Å/s is achieved.

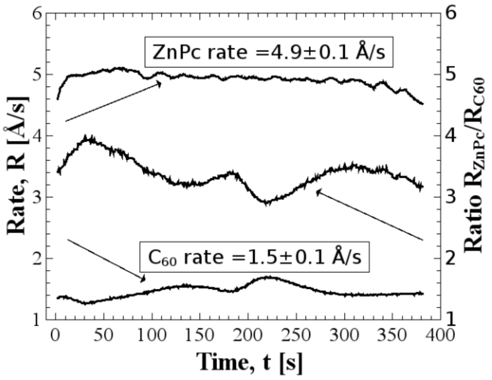


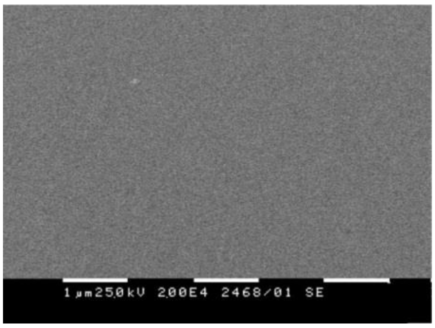
Fig. 2. Typical rates in the co-deposition process for preparation ZnPc:C_{60} composite as an active BHJ layer in organic solar cell. Right ordinate presents the R_{ZnPc} /R_{C60} ratio, calculated during the deposition process.

Surface morphology

Surface morphology SEM image of vacuum deposited C_{60} film is presented in Fig. 3. The film exhibits smooth and flat surface. This surface morphology could be more probably related to a disordered film structure.

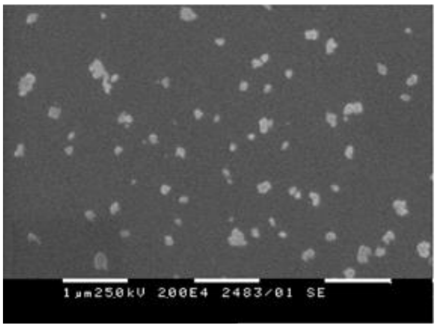
In Fig. 4 surface morphology SEM image of vacuum deposited ZnPc film is presented. This surface morphology could be more probably related to a disordered film structure with formed ZnPc agglomerate. The agglomerates of approximate 10÷30 nm size are probably formed after the film growth by recrystallization.

Fig. 3. SEM image of vacuum deposited C60 film.



Thickness: 45±3 nm.

Fig. 4. SEM image of vacuum deposited ZnPc film.



Thickness: 75±2 nm.

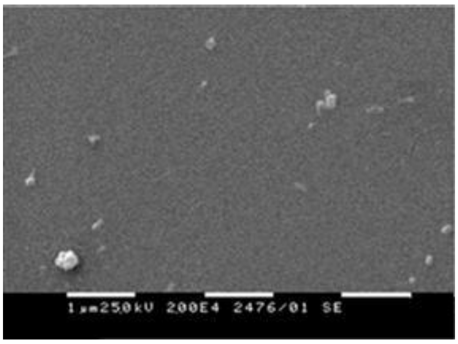


Fig. 5. SEM image of vacuum deposited ZnPc:C_{60} composite film. Thickness:147.0±0.4 nm.

Surface morphology SEM image of vacuum deposited ZnPc:C_{60} composite film is presented in Fig. 5. Again a smooth film surface with some agglomerates of approximate 10÷30 nm size is seen. In this case the concentration of the more ordered particles is less than the case of pure ZnPc. This surface morphology expresses some intermediate state between pure C_{60} and ZnPc film surfaces, which is an expected result. As the evaporation conditions are kept uniform during the whole time of deposition of about 400 s it could be expected that the surface morphology pictures could be related to the BHJ structure of the film.

Photoelectrical measurements

I-V characteristics of ITO|ZnPc|Al and ITO|PEDOT:PSS|ZnPc:C_{60}|Al structures were measured in dark, and under light illumination as described above. For sake of clarity the characteristics were plotted in semi logarithmic scale.

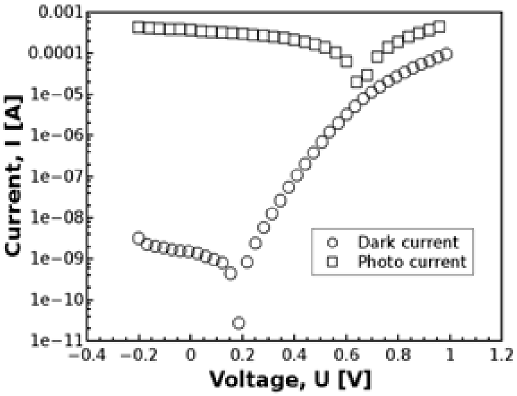


Fig. 6. *I-V* characteristics of ITO|ZnPc|Al samples measured in dark and under light exposure with light according to standard AM 1.5.

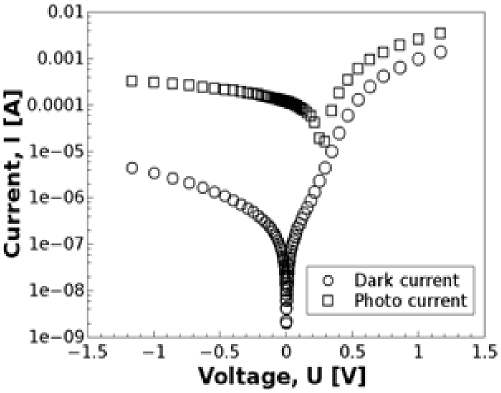


Fig. 7. *I-V* characteristics of ITO|PEDOT:PSS| ZnPc:C_{60}|Al samples measured in dark and under light exposure with light according to standard AM 1.5.

The dark *I-V* characteristic of ITO|ZnPc|Al structure (Fig. 6.) measured in both directions of the voltage scale shows typical asymmetric curve, which is clearly related to a diode behaviour. The dark current measurements indicate formation of a contact barrier at about 0.2 V. This barrier could be related to the ITO|ZnPc interface as no HTL is used. The photocurrent measured from the same structure in reverse voltage direction is higher more than 5 orders of magnitude than the dark one, and

Table1. Photoelectrical parameters of the measured structures

structure	I_{sc}	V_{oc}	FF	η	R_{sh}	R_s
	mA	mV	%	%	Ω.cm^2	mΩ.cm^2
ITO|ZnPc|Al	0.016	607	34.9	0.07	67605	735839
ITO|PEDOT:PSS|ZnPc:C_{60}|Al	0.14	398	34.4	0.44	4493	38343

the open circuite voltage (V_{oc}) of 0.6 V is measured. It should be taken in mind that the curve consists also the dark current contact barrier of 0.2 V. Therefore the final value of V_{oc} = 0.6 - 0.2 = 0.4 V could be obtained.Although the current changes more than 5 orders of magnitude under the light illumination the efficiency (η) is very low (Table 1). This effect could be related to the weak charge carrier separation on the ZnPc|Al interface. The relative high value of the shunt resistance (R_{sh}) could be related to the high resistivity of ZnPc film and the high value of the serial resistance (R_s) could be connected with the contact barriers.

Dark current characteristics of ITO|PEDOT: PSS|ZnPc:C_{60}|Al structures measured in both directions of the voltage scale are presented in Fig. 7. The weaker asymmetry of the curves comparing with the previous case could be related to the decreased contact barriers – the sample decreases his diode properties.

The difference between the dark and photocurrent in reverse direction is only 1.5 orders of magnitude but the I_{sh} increases almost an order of magnitude (Table 1). V_{oc} is about 0.4 V which could be connected with the reduced contact barrier due to the presence of PEDOT:PSS as HTL. This effect is also expressed in the reduced, more than 10 times R_s. This is a clear evidence that the PEDOT:PSS layer decreases the contact barrier. It should be mentioned here that R_{sh} decreases more than 10 times, which obviously results in lower photo generated power. As the R_{sh} could be more related to the BHJ layer than the whole solar cell structure, more optimization of ZnPc:C_{60} composite should take place. It could be expected that decreasing the C_{60} concentration will lead to an increase in R_{sh} in a way to improve the solar cell parameters.

CONCLUSION

An algorithm for determination of the mass ratio between two components of a composite material during the vacuum co-deposition process was developed. A vacuum co-deposition of ZnPc:C_{60} composite BHJ layer was obtained.

This surface morphology express some intermediate state between pure C_{60} and ZnPc film surfaces, which could evidence a formation of a composite. The photoelectrical measurements clearly display an improved photoelectrical properties of the BHJ ZnPc:C_{60} composite with respect to pure ZnPc film. The lower value of R_{sh} indicates the decreased resistivity of the BHJ layer which leads to big reduction of the photo generated power. On the base of the algorithm developed further optimization of the co-deposited BHJ ZnPc:C_{60} composite should take place.

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ПОЛУЧАВАНЕ НА ОРГАНИЧНИ СЛЪНЧЕВИ ЕЛЕМЕНТИ ЧРЕЗ СЪВМЕСТНО ВАКУУМНО ОТЛАГАНЕ ОТ ДВА ИЗТОЧНИКА

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(Резюме)

Представен е алгоритъм за определяне на масовото съотношение между компоненти при съвместно вакуумно изпарение от два източника. Алгоритъмът е демонстиран при приготвяне на органични слънчеви клетки от типа ITO|PEDOT:PSS|ZnPc:C_{60}|Al на основата на цинков фталоцианин (ZnPc). Активният органичен ZnPc:C_{60} слой, формиращ обемния хетропреход се получава при съотношение на компонентите 4.2:1. Повърхностната морфология е характеризирана чрез СЕМ. Проведените фотоелектрични измервания показват предимствата на композитния материал в сравнение със свойствата на еднокомпонентния ZnPc слой. Алгоритъмът позволява по-нататъшно оптимизиране на слънчевите клетки с обемни хетеропреходи.