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Research paper

Thermal characterization of metal phthalocyanine layers using photothermal radiometry and scanning thermal microscopy methods

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ABSTRACT

The metal phthalocyanines (MePc) were thermally investigated using photothermal radiometry (PTR) and scanning thermal microscopy (SThM). Copper phthalocyanine and lead phthalocyanine layers with different thicknesses were deposited on Si (111) wafer and on glass substrates by physical vapor deposition in a high vacuum. SThM measurements allowed the determination of local thermal conductivity (κ) of studied MePcs. This method did not require any preliminary sample preparation. The influence of the substrate thermal properties on SThM thermal signal was taken into account for estimating the true value of κ for the organic layer. For PTR investigations MePcs were coated with an opaque aluminum film. Photothermal measurements enabled determination of the in-depth κ. To complement thermal investigations of MePc layers, quantitative analysis of surface morphology properties was performed by an atomic force microscopy. The results of thermal investigations were explained on the base of different surface morphologies of examined organic layers.

1. Introduction

Recently, molecular organic semiconductors with the metal phthalocyanines (MePc) at the forefront have been entering into optoelectronic and photovoltaic applications due to promising photoconducting and semiconducting properties [1,2]. Taking advantage of their thermal and chemical stability [3], strong optical absorption [4] and ultra-efficient light emission [1], MePcs have been tested in solar cells [5,6], photosensitizers [7], and chemical and gas sensor technologies [8,9]. However, the performance of any organic device is affected by thermal effect [10]. Operating lifetime of the organic device is strongly limited, as the Joule heat cannot be released immediately. Furthermore, many processes which are important in terms of their use in photovoltaics, like charge transport, exciton decay, and recombination, are thermally activated [11–13]. All this indicates the importance of understanding the heat transport and energy dissipation in organic materials and devices. In order to increase the working stability and avoid overheating, improvement of thermal management of organic devices is crucial [14,15]. Therefore, careful thermal characterization of organic active layers is one of the milestones for future photovoltaics and sensors development.

Thermal investigations of organic materials are non-trivial for several reasons. One of them is associated with their instability due to temperature increase. Most of the dynamic thermal methods rely on a sample heating, in order to induce a temperature gradient inside the sample. As organics have low κ (less than 1 W m^{-1} K^{-1}) [16–18], large temperature gradients can occur inside the sample, causing a risk of changing the structure of the material or even destroying it. For small temperature fluctuations during measurements, the 3omega method (3ω) [19] and the photothermal radiometry (PTR) are suitable [20–23]. κ of organic layers can also be measured via time-domain thermoreflectance method (TDTR) based on the pump-probe technique [16]. The next issue concerns a proper preparation of organic samples for the selected method. Usually organics are deposited on glass or silicon. Regardless of the material, the influence of the substrate thermal properties on thermal signal should be taken into account for estimating the true value of a thin film κ. Moreover, deposition of organic layer on any substrate introduces the thermal boundary resistance (TBR), which causes a temperature discontinuity at the interface of two materials and influences the effective κ of the investigated structure [24,25]. In the 3ω method, the source of the additional TBR is a deposition of a metal wire with contact pads onto the film, acting both as a heater and a thermometer. Unlike the 3ω, the TDTR and PTR methods are contactless, which is more favorable in the case of sensitive organic structure.

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However, if the organic layer is not opaque to the illuminating laser light, an additional absorbing layer is necessary [26]. Finally, it should be noted that thermal properties measurements of sub-micron layers require suitable spatial resolution. In addition to the already mentioned methods, scanning thermal microscopy (SThM) is a technique with a proven value for investigation of thermal transport in nanoscale, but also for determination of local thermal properties [27–30].

The above-mentioned problems are probably the reason why thermal investigations of organic layers, including MePc, are in significant minority with respect to the others, like photoemission, electrical, optical or structural [31–33], while at the same time the significance of thermal investigations for these materials is commonly emphasized. There are few thermal studies on MePc layers. For κ investigation the 3ω and the TDTR methods were applied [24,25]. Jin et al. presented thermal characterization of structures consisting of alternating CuPc and metal layers [24]. In turn, M. Krzywiecki et al. measured local thermal resistance of FePc by the use of SThM with the KNT-SThM-1an probe [34]. The author points to the need of morphology investigation of examined organics, since the surface morphology and grains arrangement affected their thermal properties.

This work aims at the thermal characterization of MePc layers on samples of lead (PbPc) and copper (CuPc) phthalocyanine layers, using PTR and SThM with Wollaston probe. The goal is a determination of local κ by SThM and in-depth κ, with possible thermal boundary resistances at interfaces, by PTR technique. We propose the combination of these two methods along with atomic force microscopy (AFM) surface morphology studies for more complete thermal analysis of MePc organic layers.

2. Experimental

2.1. Samples

The objects of the study were CuPc and PbPc layers deposited on glass and silicon substrates by physical vapour deposition (PVD) in a high vacuum. Powders of the CuPc and PbPc (Sigma-Aldrich Chemie GmbH) were degassed before sublimation in order to remove residual impurities and water. The base pressure in the deposition system was 5×10^{-6} Pa and the deposition rate was kept at the level of 1 Å s^{-1}, as it was controlled by the Inficon XTC3M quartz crystal microbalance (QCM). Substrate Si (111) wafer and glass N-BK 7 were degreased with acetone in an ultrasonic bath, rinsing with deionized water and drying in a nitrogen stream.

A half of metal phthalocyanines samples deposited on glass substrates were coated with aluminum film. Aluminum films were evaporated at the base pressure of 8×10^{-6} Pa. The Al was deposited by PVD method from resistively heated crucible using aluminum rods (99.997% of purity) as a target. The thickness and deposition rate were also controlled by Inficon QCM. The deposition rate was kept at the level of < 0.02 nm/s for maintaining the Al vapors at the lowest possible temperature in order to prevent possible penetration of the Pc layer by condensing aluminum (so called pin-hole effect). Thicknesses of organic layers and aluminum coatings were measured by a profilometer and collected in Table 1.

Table 1
Basic characterization of investigated samples.

Number of sample	#1	#2	#3
MePc sample	PbPc	CuPc	CuPc
Thickness of organic layer, nm	900 ± 10	136 ± 4	500 ± 10
Substrate	N-BK 7	N-BK 7	Si
Thickness of substrate, μm	830 ± 10	830 ± 10	320 ± 10
Coating on the half of the organic surface	Al	Al	–
Thickness of coating, nm	145 ± 10	38 ± 3	–

Table 2
Reference materials used in the SThM measurements and their κ values. Calibration samples were produced by Goodfellow and Solvay companies. The preparation and characterization of reference samples was carried out in the Center for Scientific and Industrial Metrology (Trappes, France).

Reference sample	κ, W m^{-1} K^{-1}
TiAlV alloy	6.50
Vitro Ceramic	1.61
Ti	56.2
Ta	19.0
Black Acetate foil	0.33
Glass	1.20
Air	0.025
PVDF	0.13

2.2. SThM measurements

The detailed description of the SThM method and its applications can be found in review papers [27,35]. SThM measurements were performed using a Wollaston probe in Wheatstone bridge configuration combined to an AFM equipment type 2990 MicroTA from TA Instrument. The SThM measurements were performed for investigated MePc samples and for the reference materials of known κ values, presented in Table 2.

The measured signal was a heat flux from the probe to the surroundings, expressed by the power P (mW) dissipated on the probe. In order to reduce the influence of ambient temperature variations on measured signals, prior to each measurement taken on the sample surface, the signal value of the probe in air was measured, and their relative difference was then analyzed. In turn, for reducing the influence of sample surface roughness on the quality of the probe-sample contact, and therefore also on the measured signals, 10 measurements on different areas of each sample were taken and then averaged.

2.3. PTR measurements

PTR is a non-contact and non-destructive method for determining thermal properties of materials [36,37]. A modulated laser light heats a sample surface to induce a thermal response in a sample, which is then detected by an IR detector. In this experiment, a laser with 532 nm wavelength and power of 300 mW was used. The beam diameter was of 0.7 mm at $1/e^2$. The alternative temperature of the samples was estimated to be less than 1 K at 1 kHz and the DC temperature did not exceed 400 K. PTR measurements were carried out in front detection configuration (FD-PTR), meaning that the thermal excitation and the infrared radiation response is detected at the same sample surface. Detailed information about the experimental setup can be found in [38]. The amplitude and phase of the infrared signal from MePc layers were measured in frequency domain in the range from 1 Hz up to 100 kHz.

2.4. AFM measurements

For topography imaging of MePc layers and investigation of their surface morphology properties, an AFM was used. The measurements were carried out using a PSIA XE-70 microscope. The topography scan was performed in a non-contact mode using a BS Tap300Al cantilever. The Gwyddion 2.45 software was used for image processing and for quantitative determination of morphology properties.

3. Results

3.1. SThM results

For each of the measured materials the difference ΔP between probe