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Tunable optical constants of thermally grown thin porphyrin films on silicon for photovoltaic applications



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ABSTRACT

The possibility to tune optical constants of porphyrins, only by varying the core substituents of the molecules, endorse them as promising thin film materials for dye-sensitized- or hybrid molecular heterojunction- solar cells. For the design and improvement of such optical devices involving porphyrin layers, exact knowledge of the optical properties is desirable. Here, thermally grown thin films of different *meso*-tetraphenyl porphyrins (*i.e.* H₂TPP, NiTPP, and CoTPP) on silicon are assessed by spectroscopic ellipsometry and atomic force microscopy. Optical constants were determined in the near-IR to near-UV spectral range. A detailed discussion of the optical bands and the related electronic transitions is performed.

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1. Introduction

Especially porphyrin based solar cells are of current technological interest in the form of dye-sensitized solar cells [1], hybrid molecular- [2] or bulk-heterojunction solar cells [3]. Organic dye-sensitized solar cells (DSSCs) have been developed in the past 20 years and reached, nowadays, efficiencies well above 10% by using easy to handle and low thermal budget processing techniques becoming an alternative to the classical silicon-based solar cell technology [1,4]. In DSSCs typically a dye layer is bound to a nanostructured wide-band semiconductor such as titanium dioxide (TiO₂ – anatase modification). The dye molecules absorb light and in turn they inject electrons into the conduction band of the nanocrystalline TiO₂ layer. The excited state of the dye is then recovered by charge injection from redox species in the contacting electrolyte [5]. Among the various organic dyes (*e.g.* coumarins, phthalocyanines, triphenylamines, and phenothiazines), porphyrins are frequently employed photosensitizers [1]. They possess high absorption coefficients, leading to strong light harvesting abilities, with a Soret band in the 400–450 nm spectral range and Q bands in the 500–650 nm spectral range. Recently donor- π -acceptor porphyrins were studied for DSSCs, revealing that the free-base and Zn-porphyrins offer immense potential as light harvesting component of dye-sensitized nanocrystalline TiO₂ solar cells [6].

Moreover structural properties of the molecules may influence the efficiency of the solar cell and they have to be kept in mind. The first structure-performance trends such as the influence of molecular orientation of porphyrins on the TiO₂ surface in the DSSCs are reported in [7]. Since the optical and electronic properties of porphyrins can be varied by changing the molecular structure, including the size, metal center, ligands, specific side groups and conjugation, they became one of the most efficient dyes used in photovoltaic applications. In fact, the highest efficiency solar cell reported to-date ($\eta=12.3\%$) is using zinc porphyrin-based dye molecules [8] while a decade ago the best porphyrin-sensitized devices reported power conversion efficiencies in the range of 2–4% only [9]. Therefore, tuning the optoelectronic properties of the porphyrin is a fundamental step in enhancing and improving organic solar cells. This can be achieved by changing the design (*e.g.* variation of the core substituents) of the involved porphyrin molecules as well as the morphological and structural properties of the porphyrin films themselves [2]. In addition, porphyrins are used as key constituents in organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) [3].

In the present study, the effect of the core substitution on the optical constants of various porphyrin (*i.e.* H₂TPP, NiTPP, and CoTPP) films is investigated by means of the spectroscopic ellipsometry (SE) technique. Ellipsometry is a powerful optical method which has been applied successfully in the characterization of the organic photovoltaics as shown recently [10,11]. Silicon has been chosen as the substrate since well defined surface orientations can be prepared and the optical properties are well-known, so that in turn the optical

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properties of molecular layers can be obtained. The porphyrin films were prepared under vacuum conditions by the organic molecular beam deposition (OMBD) which provides great advantages like precise control on the film thickness, homogeneity, clean substrate, and environment [12]. Thin films with a nominal thickness in the range of few tens of nm were particularly considered in the view of typical thicknesses in organic solar cells. For such optical applications the device efficiency is depending on e.g. the design of the layers and their optical properties but also on the diffusion length as well as the carrier collection length, which are both in the range of 20–40 nm [13].

2. Experimental section

H₂TPP, NiTPP, and CoTPP (see Fig. 1) with a purity of 98% were purchased from Porphyrin Systems GmbH and used without further purification. The molecular axes from Fig. 1 are defined after Ref. [14]. The porphyrin films were prepared by OMBD on p-type Si(111) substrates, kept at room temperature under high vacuum conditions (base pressure $\sim 10^{-8}$ mbar). The silicon substrates covered by a native oxide of ~ 2 nm were purchased from Mateck GmbH and cleaned of contaminants by consecutively using acetone, isopropanol, and DI-water. The organic source materials were evaporated from Knudsen cells, kept at temperatures of 200 °C for H₂TPP and 225 °C for metalloporphyrins (NiTPP and CoTPP). The film thickness was *in situ* monitored using a quartz crystal microbalance which was calibrated by ellipsometry. Finally, films with the average nominal thicknesses of 33 nm for H₂TPP, 30 nm for NiTPP, and 38 nm for CoTPP, were prepared and investigated by spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).

Ellipsometry is a standard method for the analysis of the organic films, providing information on optical constants, conductivity, film structure, thickness, homogeneity or surface roughness [15]. It is a polarization dependent characterization technique, non-destructive and contact-free, that measures the change in polarization of light as a function of wavelength and angle of incidence. The ellipsometric parameters, Ψ and Δ , are measured as the ratio of the complex reflection coefficients r_p and r_s according to relation (1):

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta} \quad (1)$$

A detailed description of the SE principle and theory can be found in the following references [16,17].

In the present study the SE measurements were performed *ex situ* immediately after the film growth. The SE spectra were taken from 1.5 to 4.5 eV (12 meV steps) at different angles of incidence (AOI) between 45° and 65° (5° steps). From multiple AOI measurements there is no indication for an out-of-plane optical anisotropy. The in-plane optical anisotropy of the porphyrin films has been ruled out from the measurements performed at different azimuthal angles.

The measured optical response of the isotropic samples was modeled in the 4×4 matrix formalism [16] by the following layer structure: Si/SiO₂/porphyrin film/air. Within the chosen layer structure, the optical response of the substrate was described by the optical constants reported in the literature for Si [18] and SiO₂ [19]. The experimental ellipsometric data were simulated using the Levenberg–Marquardt algorithm [20] implemented in the WVASE software (Woollam). The nominal thicknesses of the porphyrin films have been determined in the free-absorption energy range between

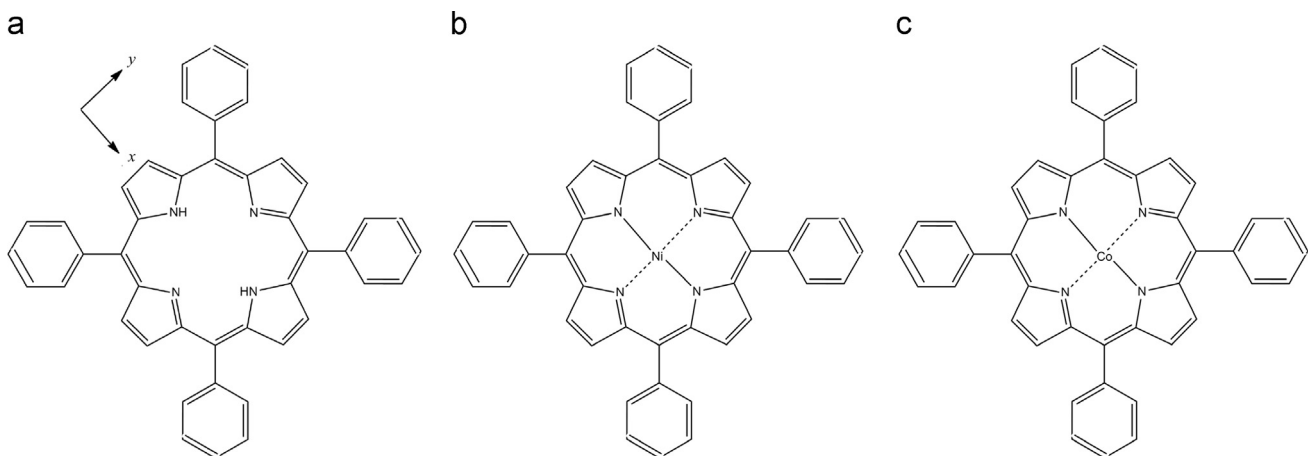


Fig. 1. Molecular structure of the *meso*-type tetraphenyl porphyrins (TPPs) investigated in this article: (a) H₂TPP, (b) NiTPP, and (c) CoTPP. The direction of the central N–H bonds of the H₂TPP molecule coincides with the x axis after [11–14].

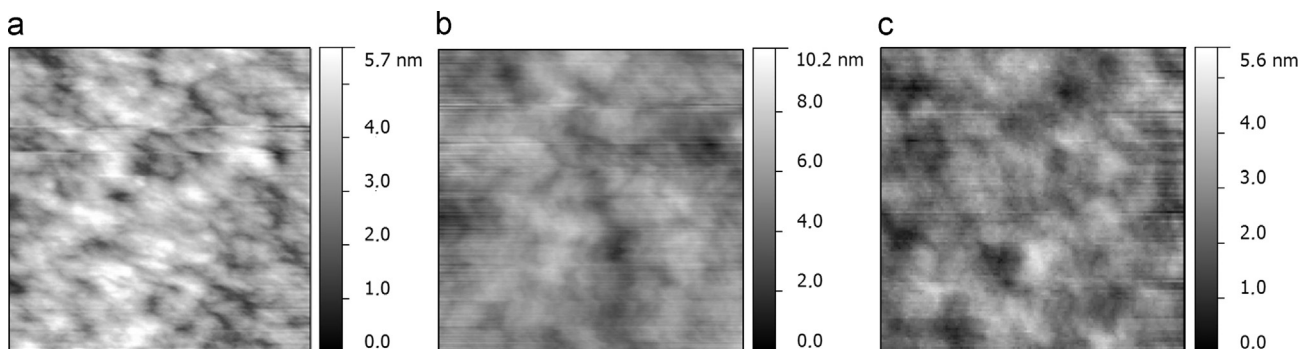


Fig. 2. The surface topographies recorded by nc-AFM for scanned areas of $0.5 \times 0.5 \mu\text{m}^2$ of (a) H₂TPP (RMS=0.7 nm), (b) NiTPP (RMS=0.8 nm), and (c) CoTPP films (RMS=0.6 nm) on Si.

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