Organic layers on silicon with potential application in hybrid solar cells


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Received 16 June 2005; accepted 18 October 2005
Available online 6 February 2006

Communicated by: Associate Editor Arturo Morales-Acevedo

Abstract

Investigations of the optical gap and the transport gap of two phthalocyanine (Pc) materials: CuPc and H\textsubscript{2}Pc, deposited on hydrogen passivated Si were performed by means of spectroscopic ellipsometry and combined valence band photoemission and inverse photoemission. The optical gaps have found to be approximately the same value for both Pcs, namely 1.75 eV, while the transport gaps have values of (2.2 ± 0.2) eV. Based on the values obtained the high similarity of these Pcs is discussed.

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Keywords: Phthalocyanine; Spectroscopic ellipsometry; Photoemission; Inverse photoemission; Transport gap; Optical gap

1. Introduction

The search for low cost alternatives to inorganic semiconductors resulted in a growing interest in organic materials. In addition hybrid organic/inorganic structures seem to offer a viable solution for photovoltaic cells and photodetectors. Promising candidates for the active layer are phthalocyanine molecules (Leznoff and Lever, 1996; Yonehara and Pac, 1996). This class of organic semiconductor materials (McKeown, 1998) possesses a high thermal and chemical stability as well as high optical absorption in the visible range. Studying these properties together with the electronic properties can help to improve the device efficiency. Therefore, the aim of this work is to present the optical and electronic properties for two representative materials of the Pc class: metal-free phthalocyanine (H\textsubscript{2}Pc) and copper phthalocyanine (CuPc).

These two materials are blue pigments used in dye industry (McKeown, 1998). Both molecules have an intrinsic optical anisotropy due to their planar structure leading to anisotropic properties also in molecular layers. The molecular orientation affects the optical absorption as well as conduction properties due to the degree in overlap of the π orbitals. Ellipsometric measurements were used to investigate the optical gap \(E_{\text{opt}}, \text{ eV}\) and the molecular orientation, while inverse photoelectron spectroscopy (IPES) combined with valence band photoelectron
spectroscopy (VB-PES) was used to probe the transport gap ($E_t$, eV). While the optical gap is related to the absorption efficiency the transport gap is relevant for the energy level alignment at the interface of distinct materials such as the molecular layer and the substrate and thus determines the transport across the interface. The transport gap $E_t$ is the minimum energy required for the formation of a separated free electron and hole pair and is found to be considerably larger than $E_{opt}$ (Hill et al., 2000). The optical gap $E_{opt}$ corresponds to the formation of a Frenkel exciton with the electron and hole on the same molecule. The calculated difference between $E_t$ and $E_{opt}$ should be close to the exciton binding energy, which can be as large as 1 eV (Hill et al., 2000).

Even though Pcs have been studied quite extensively by means of optical methods, the VB-PES-IPES combination was hardly employed for the characterization of Pcs. The most probable reasons are the low efficiency of IPES, which makes it a rather difficult technique and its low energy resolution e.g. 0.4 eV in this case. However, there are several representative examples from the literature, where the transport gap is determined in this manner. Hill et al. (2000) performed combined photoemission and inverse photoemission measurements on thin CuPc films. Taking into account polarization effects at the surface and in the bulk of the organic film they estimated the transport gap to be $(2.3 \pm 0.4)$ eV (Hill et al., 2000). Gao and Kahn (2002) determined in a similar way a transport gap of $(1.95 \pm 0.4)$ eV for ZnPc.

Previous ellipsometry studies on H$_2$Pc (Arwin and Aspnes, 1986; Debe and Field, 1991) and CuPc (Debe, 1992; Djurisic et al., 2002) considered the phthalocyanine layers as isotropic. However, the molecular orientation is influenced by various parameters during the deposition (Leznoff and Lever, 1996) such as substrate, its pre-treatment, substrate temperature during the deposition and as in the present case the pressure (Pa) in the preparation chamber.

## 2. Experimental

Organic thin films of H$_2$Pc and CuPc were grown by organic molecular beam deposition (OMBD) in high vacuum (HV-$8 \times 10^{-5}$ Pa) and ultra-high vacuum (UHV-$8.5 \times 10^{-8}$ Pa). Hydrogen passivated p-type, (111) oriented silicon provided by Siltronic AG with a doping concentration of approximately $1.5 \times 10^{15}$ cm$^{-3}$ was used as a substrate. The passivation process consists of a wet chemical etching in a solution containing HF 40%. During this procedure, the Si dangling bonds are saturated with hydrogen. Immediately after passivation, the substrates were transferred into the deposition chamber. During the deposition, the substrates were kept at room temperature. The thickness of the organic material was monitored by a quartz crystal micro-balance, which was located in the vicinity of the samples. The change in the resonant frequency of the quartz is proportional to the film thickness. The deposition rate was kept constant at approximately 0.3 nm/min.

The VB-PES and IPES measurements were performed on two UHV systems (base pressures $3 \times 10^{-8}$ Pa and $8.5 \times 10^{-8}$ Pa, respectively), each comprising an analysis and a preparation chamber. VB-PES spectra were recorded in normal emission with a hemispherical analyser and using He I radiation (21.22 eV) providing an overall resolution of 0.1 eV. The IPES experimental set-up working in the isochromat mode is a “home” built system. The fixed-energy photon detector (Prince, 1988) consists of a Geiger–Müller tube with a magnesium fluoride (MgF$_2$) window filled with a gas mixture containing ethanol and argon. The ionisation energy of ethanol and the transmission function of the MgF$_2$ provide a value of 10.9 eV as the nominal detection energy of the detector. A low energy electron gun (Erdman and Zipf, 1982) was used to produce a mono-energetic electron beam. The overall IPES instrumental resolution estimated from the width of the Fermi edge measured for an Ar sputtered nickel sample is 0.4 eV. Spectra were recorded at normal incidence with a current density in the range of $10^{-8}$ A/cm$^2$. This value is low enough in order not to damage the organic film.

The evaluation of the VB-PES and IPES spectra was performed using the diagram shown in Fig. 1. The sketch is based on experimental data recorded for the CuPc/H–Si system. Several electronic properties can be determined for silicon and CuPc. The ionisation energy (IE, eV) is evaluated by subtract-
ing the width \( W \) of the PES spectra from the excitation energy of 21.2 eV. Then subtracting the difference between the highest occupied molecular orbital (HOMO) cut-off and the Fermi level position from IE the work function \( \Phi \) is obtained. The electron affinity (EA, eV) is obtained by deducting from \( U \) the lowest unoccupied molecular orbital (LUMO) cut-off position after deconvolution measured relative to \( E_F \). In addition, rigid shifts of the secondary electron cut-off positions provide information about interface dipoles between the substrate and the molecular layer.

The ellipsometric measurements were performed ex situ immediately after removing the samples from the chamber using a variable angle spectrometric ellipsometer (VASE, J.A. Woollam Co., Inc.). No changes in the experimental spectra were recorded even after several weeks showing that the samples are very stable under atmospheric conditions. Further details of the ellipsometric measurement can be found in Gordan et al. (2004a,b).

3. Results

3.1. Optical properties

The ellipsometric measurements showed that all samples are in plane isotropic. However, the molecules have a preferential orientation along the \( z \)-axis of the film (perpendicular to the sample surface) forming uniaxial anisotropic films. Therefore, the ellipsometric data evaluation was performed taking into account a uniaxial model (Gordan et al., 2004a,b). Figs. 2 and 3 show the complex dielectric function for the \( \text{H}_2\text{Pc} \) and \( \text{CuPc} \) layers, respectively.
The shape of the absorption band centred at 2 eV (Q-band) indicates the presence of the crystalline $\alpha$-phase (McKeown, 1998) for H$_2$Pc as well as for CuPc films. Taking into account that the Q-band and B-band (centred at 3.6 eV) are $\pi-\pi^*$ transitions and are polarized in the molecular plane, an average molecular orientation can be determined from the optical anisotropy.
The samples grown in HV have an average orientation of the molecular plane with respect to the substrate at an angle lower than 45°, while for the UHV samples the molecules adopt a more standing orientation. This can be interpreted in terms of crystal orientation like a standing $b$-axis configuration for the HV films (Gordan et al., 2004b). For the UHV films, the molecular stacking axis is parallel with the substrate surface.

Considering in a first approximation that the Pc molecule is planar and the overall absorption intensity is the result of a scalar product between the electric field vector and the transition dipole, an estimate of the average orientation of the molecules with respect to the substrate can be obtained from the difference in the integral absorption perpendicular and parallel to the film surface. In the H$_2$Pc films, the average molecular orientation is at 34° with respect to the substrate. For the CuPc films prepared in HV, the average molecular orientation with respect to the Si substrate is at $\sim$40°, while for the sample prepared in UHV it is at $\sim$53° (Gordan et al., 2004b). The optical gap $E_{\text{opt}}$ positions are determined by the lowest energy peak positions of $\varepsilon_2$. The values for H$_2$Pc and CuPc are listed in Table 1.

### Table 1
Transport and optical gaps for H$_2$Pc and CuPc

<table>
<thead>
<tr>
<th>$E_t$/eV</th>
<th>$E_{\text{opt}}$/eV</th>
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<tbody>
<tr>
<td>H$_2$Pc</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>CuPc</td>
<td>2.2 ± 0.2</td>
</tr>
</tbody>
</table>

3.2. Transport gap

When estimating the transport band gap from the VB-PES and IPES combination we have to consider the rather large experimental resolution of the IPES set-up. The 0.4 eV resolution of IPES leads to a broadening and a smearing out of the features. However, we employed a mathematical method that allows the evaluation of the spectra without the contribution of the resolution. Each FWHM of a feature in the measured spectra is theoretically obtained by the convolution of two Gaussian functions. The first one represents the experimental resolution of IPES. The second one is given by the natural broadening of the states derived from solid state effects, random disorder in the film and temperature effects. Thus, by deconvoluting the IPES spectra with the Gaussian function of the experimental resolution we obtain spectra characterized only by the sample dependent broadening.

Fig. 4(a) displays the VB-PES and IPES spectra of 20 nm of CuPc on H–Si(111). The experimental data were scaled in order to be plotted in the same graph. On the left hand side of Fig. 4(a), the VB-PES experimental data and fit are shown. The three peaks present are the characteristic features for
CuPc (Hill et al., 2000). The onset position of the HOMO is taken for the determination of $E_t$. On the right hand side, the background subtracted IPES experimental data, fits and deconvolution are presented. In order to determine the LUMO peak position, the experimental data were fitted together with a polynomial background and Gaussian functions. Then the obtained peaks were deconvoluted with a Gaussian function of 0.4 eV FWHM accounting for the experimental resolution. The LUMO onsets were determined with respect to the Fermi level by a linear extrapolation of the low energy edge of the obtained LUMO feature. The fit of the background subtracted experimental data is included as well as the deconvoluted peaks in the case of the IPES spectra. The transport gap determined as the difference between the onset positions of LUMO and HOMO is found to be $(2.2 \pm 0.2)$ eV. This value is in good agreement with the one determined by Hill et al. (2000) using VB-PES-IPES $(2.3 \pm 0.4)$ eV, but somewhat larger than the one determined by cyclic voltammetry (Simon and Andre, 1985) $(1.71–1.84$ eV). However, it is important to note that the determination of the transport gap in our case is different from the one employed by Hill et al. (2000). Their evaluation is based on the peak-to-peak difference. From that value they subtract the vibrational contribution and the polarization energy in order to obtain the transport gap mentioned above.

In Fig. 4(b), the energy band diagram at the CuPc H–Si interface is displayed. More details about the interface formation can be found in Gorgoi and Zahn (2005). The electronic properties of 20 nm of CuPc are defined by the following values: $\text{IE} = (4.82 \pm 0.07)$ eV, $\Phi = (3.88 \pm 0.07)$ eV and $\text{EA} = (2.58 \pm 0.2)$ eV. An interface dipole of $(0.34 \pm 0.07)$ eV is measured as well. The onset positions of the HOMO and LUMO were employed in order to sketch the energy band diagram and to calculate these values. In the case of H–Si(111), the onset position of the VBM was taken into consideration for determining $\text{IE} = (5.02 \pm 0.07)$ eV and $\Phi = (4.22 \pm 0.07)$ of the surface. The VBM is obtained in the direction perpendicular to the (111) plane of silicon. However, the conduction band minimum is not situated in the same direction (Mönch, 1995). The conduction band (CB) position of H–Si(111) was determined by IPES and it represents a local minima in the energy scale of the unoccupied states of the hydrogen passivated silicon surface.

Similarly, for H$_2$Pc Fig. 5(a) displays the VB-PES and IPES spectra for 20 nm of organic material deposited on H–Si(111). When compared to CuPc we observe that the spectra are quite alike. This is expected, since the central metal atom has a small contribution to the low binding energy HOMOs and LUMOs (Rocco et al., 1990). The transport gap is estimated in the same manner as

![Fig. 5. (a) VB-PES (left hand side) and IPES (right hand side) spectra of 20 nm of H$_2$Pc on H–Si(111); a polynomial background was subtracted from the IPES spectrum; (b) energy band diagram for H$_2$Pc/H–Si system.](image-url)
described for CuPc and has a value of \((2.2 \pm 0.07)\) eV for H\(_2\)Pc. It is not surprising that the \(E_t\) for both materials have the same value, since we have shown before that the optical gaps have approximately the same value as well. Fig. 5(b) contains the energy band diagram for the H\(_2\)Pc/H–Si system. The electronic properties that characterize H\(_2\)Pc are \(IE = (4.96 \pm 0.07)\) eV, \(\Phi = (4.04 \pm 0.07)\) eV and \(EA = (2.74 \pm 0.2)\) eV. Additionally, an interface dipole of \((0.18 \pm 0.07)\) eV is measured.

When evaluating the obtained electronic properties of the two Pcs, we observe slightly lower \(IE\), \(\Phi\) and \(EA\) values for CuPc than for H\(_2\)Pc. The difference amounts to approximately 0.15 eV. This is expected when taking into account the electron affinity of Cu (1.22 eV) (Hotop and Lineberger, 1975; Bilodeau et al., 1998) which is lower than the EA of H\(_2\)Pc. Thus the addition of a Cu atom to the H\(_2\)Pc molecule brings additional charge and decreases the overall EA of the resulting molecule (CuPc).

Furthermore, the barrier height for holes at both interfaces is quite small, having a value of approximately 0.1 eV. This is rather promising for applications, since transport over the interface depends on the barrier height (Mönch, 1995).

The difference between \(E_t\) and \(E_{opt}\) is related to the exciton energy and has a value of approximately 0.4–0.5 eV for both materials, CuPc and H\(_2\)Pc. In previous reports, \(E_{opt}\) was used to estimate the band alignment at interfaces. Since exciton binding energies for CuPc and H\(_2\)Pc have such large values, any evaluation of transport phenomena in Pcs using \(E_{opt}\) in the estimation would result in a large error.

4. Summary

We have determined the optical and electronic properties of CuPc and H\(_2\)Pc deposited on H–Si(111). The organic materials are highly similar. They both present optical in-plane isotropy and out-of-plane anisotropy. The determined molecular orientation is similar as well. Surprisingly they have the same optical gap of about approximately 1.75 eV. Moreover, their transport gaps are identical and have a value of \((2.2 \pm 0.2)\) eV. A summary of the determined values is shown in Table 1. Such analogous behaviour of the Pcs is mostly due to the weak contribution of the copper atom to the HOMO and LUMO.

Acknowledgements

The authors acknowledge the Deutsche Forschungsgemeinschaft, Graduiertenkolleg 829 “Akkumulation von einzelnen Molekülen zu Nanostrukturen”, and the EU funded Human Potential Research Training Network DIOIDE (Contract No.: HPRN-CT-1999-00164) for the financial support.

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