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Spectroscopic ellipsometry of metal phthalocyanine thin films

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Optical functions of cobalt phthalocyanine, nickel phthalocyanine (NiPc), and iron phthalocyanine (FePc) have been determined by use of spectroscopic ellipsometry in the spectral range 1.55–4.1 eV (300–800 nm). The samples were prepared by evaporation onto glass and silicon substrates. The optical functions were determined by point-to-point fit. Absorption spectra were also measured. The index-of-refraction data for NiPc and FePc are reported for the first time to our knowledge. Good agreement with the experimental spectra was obtained for all three materials. © 2003 Optical Society of America

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1. Introduction

Phthalocyanines are porphyrin derivatives that are characterized by high degrees of symmetry, planarity, and electron delocalization.¹ Phthalocyanines (Pcs) have attracted much attention for applications in organic optoelectronic devices such as organic solar cells,^{1–3} in organic field effect transistors,⁴ in organic light-emitting diodes in which Pcs can be used as a hole transport layers^{5,6} or emitting layers⁷; and in gas sensors.^{8,9} For modeling and design of optoelectronic devices, the optical function of each layer should be known. Optical properties of solids are usually described in terms of the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ or the complex index of refraction $N(\omega) = n(\omega) + ik(\omega)$. Copper phthalocyanine (CuPc) has been the most widely studied metal Pc. Dielectric functions and indices of refraction of CuPc were studied experimentally by use of reflectance and transmission measurements,¹⁰ absorption coefficient measurement with Kramers–Kronig analysis,¹¹ and spectroscopic ellipsometry.^{12,13} Unlike

CuPc, other metal Pcs have not been extensively studied. Investigation of cobalt phthalocyanine (CoPc) by spectroscopic ellipsometry has been reported.¹⁴ Absorption spectra of various Pc films,^{15–17} as well as vapor phases and solutions in different solvents,^{18,19} have also been reported.

The growth and morphology of the various Pc films have been extensively studied.^{20–35} Pc films can exist in several crystalline polymorphs. Most common polymorphs are metastable α and stable β phases. The main differences between polymorphs lie in the tilt angle of the molecules within the columns (stacks of molecules with molecular planes parallel to one another) and the mutual arrangement of the columns. Transformation from phase α to phase β by exposure to solvent vapors^{25,29,30} or by annealing or deposition at higher temperature^{26–28,31,32} has been reported. The absorption spectra of different polymorphs of the same Pc compound differ significantly.^{15,27,28} The polymorphism of Pcs significantly influences the preferred orientation in Pc layers. The substrate also seems to play a role in the orientation of the deposited films.^{21–24,26} It has been demonstrated that different Pcs show evident isomorphism with one another²³ and that deposition on mica at temperatures above 400 K results in oriented films.^{23,24} Wachtel *et al.*²⁴ found that the stability of the films may be substrate dependent and that lithium Pc films deposited on glass substrates at room temperature were stable over several months, whereas those on NaCl substrates showed marked changes when they were exposed to ambient conditions. For low-temperature substrates, quasi-epitaxial growth of thin fluorine bridged aluminum

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Pc polymer by molecular-beam epitaxy was obtained on alkali halide substrates, whereas epitaxial growth did not occur on silicon and quartz.²¹ Oriented films with two different *b*-axis (stacking axis) orientations, depending on the substrate's temperature, have been grown on copper substrates.^{12,33} For Si substrates maintained at room temperature, the preferred orientation of evaporated CuPc films less than 100 nm thick is in the [200] direction, with the α form dominant.²⁶ With increasing thickness, randomization of the orientation of crystallites occurs; the α form is still prevalent.²⁶ For CuPc films deposited on glass substrates, the preferential orientation of the crystallites appeared to depend on the deposition rate and on whether the substrate was rotating ([110] orientation) or nonrotating ([100] orientation).²² Bayliss *et al.*³² reported that the α form of the metal-free Pc H₂Pc deposited on microscope slides at room temperature consists of small spherical particles that are randomly oriented, whereas oriented domains in the films have been found only for the β form obtained by annealing the α form. The β form obtained by direct evaporation onto substrates heated to 330 °C showed elongated crystallites similar to those in the β form obtained by annealing, but randomly oriented.³² Highly oriented CuPc film fabricated by molecular-beam deposition onto quartz glass substrates at low deposition rates has been demonstrated.³⁴

We report spectroscopic ellipsometry measurements of CoPc, nickel phthalocyanine (NiPc), and iron phthalocyanine (FePc) thin films deposited on glass and silicon substrates at room temperature. Because the deposition is performed at room temperature, we expected that the films would be polycrystalline and predominantly of the α form. The spectroscopic ellipsometry measurements were performed in the spectral range 1.55–4.1 eV (300–800 nm). Samples were modeled as isotropic layers, as was reported to be adequate for CuPc samples less than 80–100 nm thick.³⁶ Although each Pc molecule has an intrinsic anisotropy that is due to its planar structure, for random orientation of crystallites in a polycrystalline film an isotropic model is sufficient. Atomic-force microscopy (AFM) and absorption measurements were also performed. The samples for absorption measurements were deposited onto quartz substrates.

The paper is organized as follows: in section 2, experimental details are described, and Section 3 presents results and discussions. Finally, conclusions are presented in Section 4.

2. Experimental Details

Pc powders were purchased from Strem Chemicals. First, silicon substrates were cleaned in deionized (DI) water by a standard four-cycle dump–rinse procedure. After that, the wafer was cleaned for 10 min in an H₂SO₄:H₂O₂ bath at 120 °C. Another four-cycle dump–rinse in DI water was performed, followed by HF cleaning (HF:H₂O 1:50) for 30 s to remove native oxide. After rinsing in DI water and drying, the wafers were immediately loaded into an

evaporator to minimize formation of another oxide layer. Microscope slide glass and quartz substrates were cleaned in an ultrasonic bath for 30 min, rinsed with DI water, and dried in flowing nitrogen. Before cleaning, the back side of the glass substrate was roughened to suppress back side reflections for spectroscopic ellipsometry (SE) measurement. For absorption and AFM measurements, the films deposited on quartz substrates were used. The films were evaporated in high vacuum. The sample holder can hold up as many as four substrates, so the films fabricated on microscope slides, silicon, and quartz were deposited in the same deposition process. Pressure during evaporation was of the order 10^{−4} Pa. The evaporation rate was 0.1–0.2 nm/s. The distance from source to film was ~23 cm to ensure uniformity of film thickness, and the substrate holder could be rotated. The thickness of the films was controlled by a quartz thickness monitor.

The film thickness was measured by a step profiler. Pc films are absorbing in the spectral region of interest. Absorption is weak in the 450–550-nm spectral region, but assuming a Cauchy model for the refractive index and disregarding the coefficient of extinction in this spectral region can cause errors in the thickness determined from fitting of SE data. The film thickness was also verified by AFM. A multi-mode scanning-probe microscope from Digital Instruments was used for AFM measurements. The thickness was measured at 10 points along the step to minimize the influence of possible errors caused by variation in thickness around the step. In addition to revealing film thickness, AFM also yielded a surface-roughness estimate. The rms surface roughness in all films was below 3.5 nm; the mean roughness was below 2 nm. The film thickness was 48 nm for CoPc, 56 nm for FePc, and 45 nm for NiPc.

Absorption measurements were performed on a Perkin-Elmer Lambda 20 UV/Vis spectrophotometer. The SE data in the 300–800 nm spectral range were measured with a Jobin Yvon UVISSEL phase-modulated ellipsometer. Phase-modulated ellipsometers are comparable to the more frequently used rotating analyzer ellipsometers in terms of attainable precision.³⁷ The incidence angle used was 70°. The samples exhibited good uniformity, which we verified by performing measurements at different areas of the sample on both glass and silicon substrates. Also, the samples did not exhibit any in-plane anisotropy, as we verified by rotating the sample 90° and repeating the measurement. Point-by-point fitting of the measured spectra was performed. We used a simulated annealing algorithm to fit the data.³⁸ The fitting was performed simultaneously for glass and silicon substrates. The objective function used was

$$F_i = [\Phi[\tan(\Psi)]_{\text{glass}} + \Phi[\tan(\Psi)]_{\text{Si}} + \Phi[\cos(\Delta)]_{\text{glass}} + \Phi[\cos(\Delta)]_{\text{Si}}]_i + \gamma_{i,i-1}, \quad (1)$$

$$\Phi(X) = (X^{\text{exp}} - X^{\text{calc}})^2, \quad (2)$$

where i denotes the i th experimental data point, the subscripts glass and Si denote glass and silicon substrates, respectively, and the superscripts exp and calc denote experimental and calculated data. γ is an optional penalty function that can be introduced to ensure the smoothness of the n and k obtained by limiting the allowed difference between values obtained in current (i) and previous ($i - 1$) data points. We obtained this difference in the following manner: If the difference between n and k values in current and previous data points was larger than the specified allowed difference, γ was set to a large positive constant.

Otherwise, γ was set to zero. Because of the existence of multiple solutions, the use of such a penalty function to prevent unphysical abrupt changes in n and k is advisable. We determined the refractive indices of the substrates from the SE measurements of the substrates, instead of taking the data from the material database, to ensure improved accuracy of the determined n and k of the Pc films. For Si substrates, fitting with and without a native oxide layer was performed. There was no significant difference between the results obtained in these two cases. The result of simultaneous point-to-point fitting for both substrates shows somewhat inferior agreement with the experimental data compared with point-to-point fitting for one substrate only. However, reliability of the data obtained by simultaneous fitting for both substrates is considerably improved compared with data obtained by fitting for only one substrate because there are two unknowns and four conditions that need to be satisfied.

Correction for surface roughness was not made because individual points yield different thickness values for a rough layer. Fixing the thickness of the rough layer to the value averaged over a wavelength resulted in an inferior fit. We also attempted to model the optical functions of the Pc layer and then to fit the thickness of the Pc layer and the thickness of the rough layer. However, although numerous models of the optical functions of inorganic semiconductors are available, for organic materials the choice is typically limited to the Lorentz oscillator model and its modifications^{39,40} or the Forouhi-Bloomer model.⁴¹ It was shown previously that the conventional Lorentz model is inadequate for modeling optical functions of organic materials.^{39,40} The Forouhi-Bloomer model was used only in a very narrow spectral range (365–564 nm) for a material that exhibited a single peak in the spectral range investigated.⁴¹ We attempted to use both the conventional Lorentz model and its modifications, with and without surface-roughness correction. In all cases, agreement with the experimentally determined $\tan(\Psi)$ and $\cos(\Delta)$ was inferior compared to that from point-to-point fitting. Therefore, here we present the results of optical functions obtained by point-to-point fitting without surface-roughness correction. We improved the reliability of the data by fitting the data for films on two substrates simultaneously. We also verified the quality of the result obtained by comparing the

positions of the peaks in the calculated extinction coefficient spectrum with the measured absorption data.

3. Results and Discussion

Pc films grown upon room-temperature substrates typically consist of small spherical particles and are predominantly of α modification^{26,32} or possibly of the x form.²⁵ When the substrate temperature is increased, the size of the crystallites increases, some preferential ordering in neighboring domains begins,²⁵ and finally at higher temperatures the β form is obtained.³² Deposition at temperatures below room temperature results in significantly smoother films.^{25,35} Vincett *et al.*³⁵ believed that the films were in the α form, though at temperatures below -50 °C the films may have been partially amorphous. Brinkmann *et al.*,²⁵ however, stated that films grown at temperatures of 5 °C– 25 °C have disordered, i.e., close to amorphous, structures based on diffuse diffraction rings. Pan *et al.*⁴² have found that vanadyl Pc films deposited at room temperature and exposed to flowing nitrogen for 50 h are partially amorphous. In a previous analysis of the optical functions of CuPc by variable-angle spectroscopic ellipsometry, Debe¹² investigated Pc films grown at 0 °C and 70 °C, which he assumed were well oriented, and deduced the approximate optical functions that correspond to parallel and perpendicular orientation with respect to stacking axis b . The possibility that the film deposited at low temperature may not have been well uniaxially oriented has been acknowledged,¹² but the possibility of phase change or of amorphousness of the films grown at low temperature has not been considered. In the research reported here, all the films were grown upon room-temperature substrates, so it is reasonable to assume that the films consist of polycrystalline, predominantly α phase domains with little or no preferential orientation among the neighboring domains. Because the film thickness in all cases is less than 80–100 nm, we have considered the films to be isotropic.³⁶ For films 100–150 nm thick, an isotropic inner layer and an anisotropic outer layer should be assumed, whereas a film thicker than 150 nm can be treated as a single homogeneous anisotropic film.³⁶

Figures 1–3 show $\tan(\Psi)$ and $\cos(\Delta)$ for CoPc, FePc, and NiPc films, respectively, deposited onto glass and silicon substrates. Figure 4 shows the absorption spectra for CoPc, NiPc, and FePc. In the spectral region investigated, two distinct absorption bands can be observed, a band near 2 eV (620 nm; Q band) and one near 3.5 eV (350 nm; B or Soret band). Both bands have been assigned to $\pi \rightarrow \pi^*$ transitions of the macrocyclic π system consisting of C and N atoms.^{11,13,18} The excitons that contribute to the absorption in these two bands are shown to be independent in H_2Pc .⁷ There is little difference among the visible spectra of various metal Pcs. However, metal-dependent absorption bands can be observed near the infrared spectra of Pcs.¹⁸ Also, it has been suggested that both Q and B bands can be

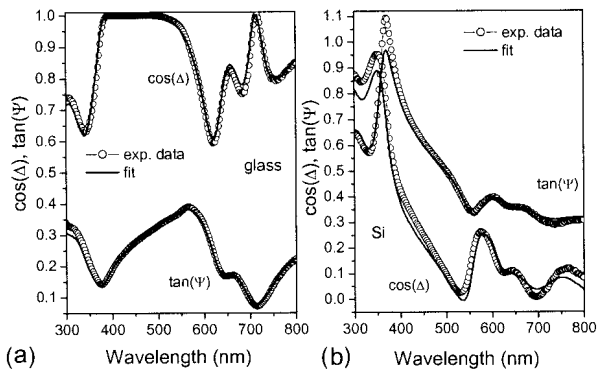


Fig. 1. $\tan(\psi)$ and $\cos(\Delta)$ for CoPc films on glass and silicon substrates. The fit is a point-to-point fit; (a) glass substrate, (b) silicon substrate.

influenced by the metal-to-ligand charge-transfer bands in CoPc (Ref. 14), and the existence of a charge-transfer band at the red edge of the Q band has been proposed. However, based on the small difference of the shift of absorption peak on the low-energy side of the Q band of CuPc in solvents of different polarities (dimethyl sulfoxide and 1-chloronaphtalene),¹⁸ it is reasonable to conclude that the charge transfer does not play a significant role in transitions on the low-energy side of the Q band. The exact identification

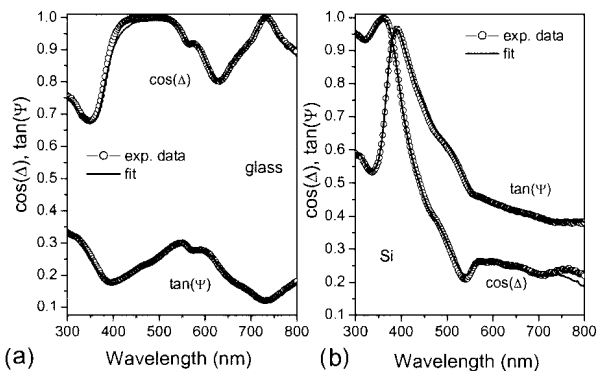


Fig. 2. $\tan(\psi)$ and $\cos(\Delta)$ for FePc films on glass and silicon substrates. The fit is a point-to-point fit.

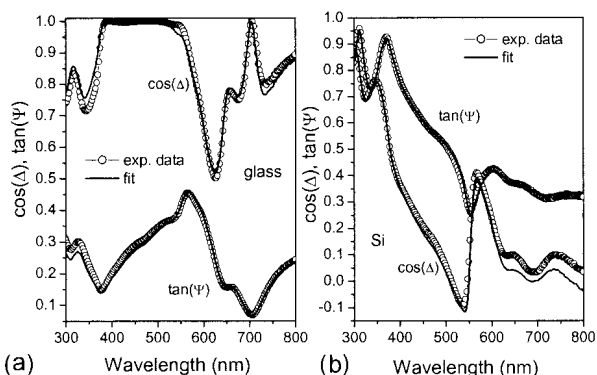


Fig. 3. $\tan(\psi)$ and $\cos(\Delta)$ for NiPc films on glass and silicon substrates. The fit is a point-to-point fit: (a) glass substrate, (b) silicon substrate.

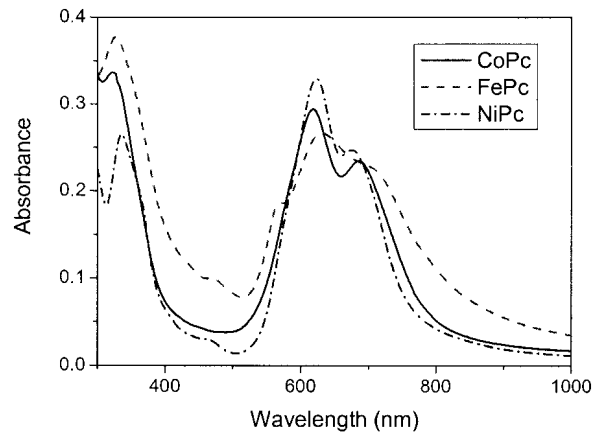


Fig. 4. Absorption spectra of CoPc, FePc, and NiPc.

of the origin of the observed peaks in the absorption spectrum of a Pc material is rather complex. *Ab initio* calculations of Pc molecules have been performed, and the calculated results are in good agreement with vapor phase spectra.⁴³ However, the spectra of solutions and thin films in which interactions between individual molecules play a role are inherently more complicated.

Figure 5 shows the real and imaginary parts of the indices of refraction of CoPc, FePc, and NiPc. Good agreement between the peak positions in the calculated extinction coefficients and the measured absorption spectra can be observed. Chen *et al.*¹⁴ determined the index of refraction of CoPc films on silicon by spectroscopic ellipsometry in the spectral region from 550 to 800 nm. Their extinction coefficient and absorption coefficient data show three peaks in this spectral region, and the value of the extinction coefficient is greater than 0.5 over the entire region, although it should be low at 550 and 800 nm according to absorption measurements reported in the literature that consistently have shown only two peaks.^{15,17} This difference may be due partly to the very thick film (greater than 600 nm) investigated by Chen *et al.*¹⁴ It has been shown that for CuPc an anisotropic model is needed for analysis of

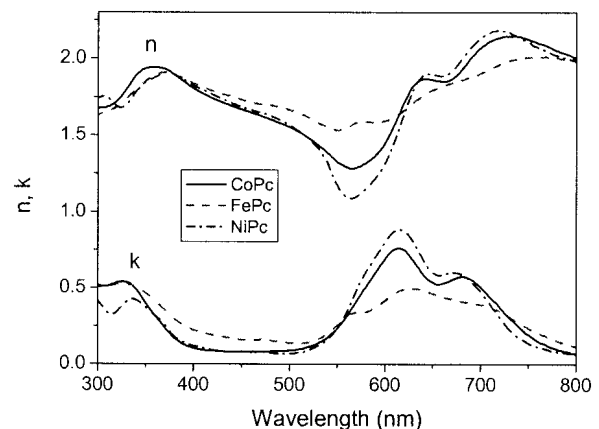


Fig. 5. Real (n) and imaginary (k) parts of the index of refraction of CoPc, FePc, and NiPc.

the ellipsometry data of films thicker than 150 nm. Lucia and Verderame¹⁵ identified two peaks in the *Q* band of the absorption spectrum of CoPc, located at 1.82 and 2.01 eV (680 and 616 nm). Davidson¹⁷ identified peaks at 1.82 and 1.98 eV (680 and 626 nm) in the *Q* band and at 3.79 eV (327 nm) in the *B* band. Our results are in good agreement with previously reported absorption spectra and with the absorption spectrum measured by us. We observed peaks at 1.82 eV (680 nm) and 2.02 eV (615 nm) in *k* derived from SE and at 1.80 eV (688 nm) and 2.01 eV (618 nm) in the absorption spectrum. In the *B* band we observed peaks at 3.81 eV (325 nm) in *k* and of 3.84 eV (323 nm) in absorption.

For FePc, no previous data on the index of refraction were reported to our knowledge. Absorption spectra for FePc have been reported,^{16,17} and three peaks can be observed in the absorption spectra. Davidson¹⁷ obtained peaks at 1.73 eV (717 nm), 1.98 eV (626 nm), and 2.19 eV (566 nm) in the *Q* band and peaks at 3.51 eV (353 nm) and 3.83 eV (324 nm) in the *B* band. Our results show maxima in the extinction coefficient at 1.74 eV (713 nm), 1.98 eV (625 nm), and 2.18 eV (570 nm) in the *Q* band and wide structure in the *B* band with a maximum at 3.81 eV (325 nm), whereas in the absorption spectrum we observe peaks at 1.73 eV (717 nm), 1.96 eV (631 nm), 2.18 eV (568 nm), and 3.79 eV (327 nm), is in good agreement with the absorption spectra reported in the literature.

Also for NiPc, we are not aware of any previous study of the complex index of refraction. Godlewski *et al.*⁴⁴ obtained an absorption spectrum showing a two-peak structure and identified four transitions in the *Q* band of NiPc, located at 1.76 eV (704 nm), 1.83 eV (678 nm), 1.98 eV (626 nm), and 2.02 eV (614 nm). Absorption measurements by Lucia and Verderame showed absorption maxima at 1.85 eV (670 nm) and 1.98 eV (626 nm), in good agreement with our results showing peaks at 1.84 eV (673 nm) and 2.02 eV (615 nm) in the *Q* band and 3.70 eV (335 nm) in the *B* band. In the absorption spectrum, peaks at 1.84 eV (674 nm), 1.99 eV (623 nm), and 3.69 eV (336 nm) can be observed. However, the refractive-index minimum obtained near 2.19 eV (566 nm) is the lowest among the Pc films measured. There are several likely reasons for this observation. One could be surface roughness of the film. However, NiPc was the smoothest film obtained (rms roughness, 2.4 nm; mean roughness, 1.7 nm), so it is not likely that surface roughness is causing the difference from other metal Pcs investigated. It has also been proposed that there are differences in refractive indices at film–air and film–glass interfaces in NiPc films.⁴⁴ The second reason is possible anisotropy of the films. The refractive-index data determined by Schechtman and Spicer¹¹ for a CuPc film with thickness of 23–45 nm grown at room temperature upon LiF substrates also show a dip in the refractive-index values to below 1.0 in the spectral region 2–2.5 eV (495–620 nm). This probably indicates a certain degree of preferential ordering in their samples, which is not surprising

for alkali halide substrates.²¹ No in-plane anisotropy was detected when the sample was rotated and the ellipsometry measurement repeated, but this does not rule out the presence of anisotropy in the *z*-axis direction. Unfortunately, because the films are not likely to be ideally ordered, it is not possible to determine their anisotropy unambiguously. Further investigations are needed to resolve this issue.

4. Conclusions

Optical functions of CoPc, NiPc, and FePc thin films have been determined by use of spectroscopic ellipsometry in the spectral range 300–800 nm. The films are likely to be polycrystalline with randomly oriented crystallites, so an isotropic model of the sample was adopted. The optical functions data were determined by simultaneous point-to-point fits of $\tan(\psi)$ and $\cos(\Delta)$ measured for films deposited upon glass and silicon substrates. Excellent agreement between experimental and calculated $\tan(\psi)$ and $\cos(\Delta)$ curves was obtained for all three materials. The agreement between the positions of the maxima in the imaginary part of the index of refraction and the absorption spectra reported in the literature and measured by us was good for all materials.

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