

Stability of Organic Thin Films on Inorganic Substrates: Prototype Studies Using Metal Phthalocyanines

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Thin films of metal phthalocyanines (PbPc and RuPc) on inorganic substrates (Ag, Pt, Cu, Au, Al₂O₃ and AgI) in the submonolayer and monolayer range were investigated. Their chemical compositions and electronic and dynamic structures were characterized by means of photoemission and vibrational spectroscopy, with particular emphasis on the influence of the film/substrate and film/gas phase interfaces. The results indicate that RuPc surfaces are always unstable in air because of an energetically favourable oxide formation involving the central (Ru) atom. Lead phthalocyanine is more stable. Lead oxides are formed only after exposing thin films prepared under ultra-high vacuum to pure oxygen. Even for PbPc, decomposition was observed at certain substrate/film interfaces: organic fragments were found in the submonolayer range on platinum substrates, an exchange of the central atom on copper substrates and catalytic decomposition of organic films on gold substrates after storage in air. Chemically perfect films without decomposition were found on Al₂O₃, AgI and Ag substrates. The results are discussed by taking into account the energetic structure of interfacial electronic states.

Keywords: Interfacial analysis; XPS; UPS; HREELS; FTIR; phthalocyanines

INTRODUCTION

The understanding and control of interfacial properties between metal-organic thin films and inorganic substrates requires a detailed knowledge of the atomic composition, the local chemistry, the geometric and electronic structures and the optical properties involved. This type of interface is of primary interest in hybrid molecular electronic devices and, in particular, in the application of sensors. Well characterized interfaces of phthalocyanine (Pc) thin films in particular are of great importance, both in basic research and in many existing and future practical applications such as in molecular electronic¹⁻³ or non-linear optical devices,⁴ organic transistors,⁵ organic photovoltaic or solar cells,⁶⁻⁸ sensors⁹⁻¹⁴ and

catalysts.¹⁵ We therefore investigated systematically the stability and stoichiometric composition of 'prototype' metal-organic lead phthalocyanine (PbPc) compounds on 'prototype' inorganic substrates.

The 'prototype' metal-organic compounds used were the thermally stable, vacuum sublimable and crystallizable PbPc and RuPc. Below a critical sublimation temperature, T_{crit} , these molecules can be sublimed from a Knudsen cell with negligible thermal decomposition.¹⁶ The physical and chemical properties of this class of organic material have been reviewed recently.¹⁷

The 'prototype' inorganic substrate materials used were the covalent semiconductor Si, the insulating ionic compounds SiO₂ and Al₂O₃, the ionically conducting compound AgI and the

metals Au, Ag, Pt and Cu. The inorganic substrates Si and SiO₂ are of particular interest in utilizing common microelectronic technology to prepare organic/inorganic sandwich structures. The metals Cu, Ag, Au are commonly used to prepare ohmic and Schottky contacts in organic solar cell fabrication.

This paper focuses on thermodynamic stability, electronic structure, chemical composition and decomposition products in the submonolayer range between phthalocyanines and the gas phase ('interface 1') and between phthalocyanines and the different substrates ('interface 2'). In the context of systematic studies at interface 1, we also examined the influence of the ambient gas on the stability of thin films. For this purpose we first investigated film structures under ultra-high-vacuum (UHV) conditions and then exposed these films to different gases or ambient air with the aim of characterizing irreversible and reversible reactions with variations in gas pressure. The latter are of particular interest for gas sensor applications.⁹⁻¹⁴

Metal phthalocyanines are particularly suitable for systematic studies by exchanging the central metal atom and thereby varying the metal's s-, p- or d-state contributions with their characteristic energetic positions relative to the 'intrinsic' molecular orbitals of the conjugated π -system (Fig. 1). As a result, we expect the electronic conductivities, optical properties, and chemical reactivities to vary systematically with the central metal atom. This allows us to tailor thin-film structures, provided that the interfacial chemistry between the metal-organic compounds and the

substrates or the gas phase is not dominated by selective decomposition with the latter being determined specifically by the particular central metal atom. The organic molecules must therefore be stable in the submonolayer range and should not undergo uncontrolled chemical reactions with the substrate or the gas phase. This stability is important in separating the specific gas-organic film interaction from instabilities caused by decomposition or reactions with decomposition products. The latter behaviour was demonstrated to cause non-reproducible conductivity changes for RuPc films, whereas for PbPc films the particular gas interaction could be investigated in detail. Instabilities will contribute even more when the organic material is used as an active gate material in microelectronic devices for sensor applications.

The interface 2 properties between the different metal-organic compounds and different substrates such as insulators, semiconductors, ionic conductors and metals used in this work are expected to depend not only on the electronic properties of the organic material, but also strongly on the local chemistry and electronic structure, i.e. the energetic position and symmetry of electronic states of the inorganic substrates. To illustrate this, characteristic electronic structures of some substrates and of phthalocyanine are shown schematically in Fig. 2.

The covalent bonding in silicon substrates leads to chemically highly reactive dangling-bond surface states in the bandgap. These surface states are located in the valence and conduction band range, respectively, for ideally insulating compounds such as SiO₂ and Al₂O₃ and for the ionic

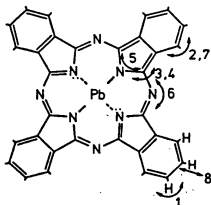


Figure 1. Geometric structure of metal (here Pb) phthalocyanines with simplified representation of some characteristic vibrational modes considered in this paper.

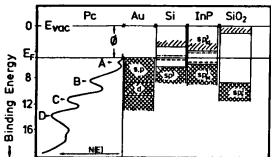


Figure 2. Schematic presentation of electronic charge distributions in the valence band of Pcs [N(E), left] and of corresponding electronic states including surface states in the band gap [(dash-dotted lines), right] for different substrates considered in this paper.

conductor AgI. Formation of lattice defects in the oxides may, however, introduce electronic states in the gap and thereby make these interfaces chemically reactive too. The metal surfaces are characterized by their different s, p and d electronic contributions in the conduction band range, their work functions and their metallic surface states. The energetic position and symmetry of surface states determines the chemical reactivity at the interface and hence its tendency to form fragments during deposition of large organic molecules.

In these studies, x-ray photoelectron (XPS) and ultraviolet photoemission spectroscopy (UPS) were used to determine the effective oxidation state of the central atom, the elemental composition of phthalocyanines and the electronic structure of both the metal atom's states and the π -system's contributions in the valence band range. Characteristic vibrational modes of phthalocyanines and their decomposition products were determined by surface-sensitive high-resolution electron energy-loss spectroscopy (EELS) and bulk-sensitive Fourier transform infrared (FTIR) spectroscopy.

In this paper we demonstrate that stoichiometric PbPc thin films and structures can be prepared on Al_2O_3 , AgI and Ag substrates, all of which can therefore be used in molecular electronic devices or in sensor applications to monitor gases such as NO_2 and O_2 . Details of the sensor properties will be published elsewhere.¹⁸ The results also indicate that PbPc/metal interfaces show instabilities and structures which are determined by the catalytic activity of the metal atoms and the structural stability of the phthalocyanine. In a subsequent paper we shall demonstrate that ideal PbPc/ SiO_2 /Si thin-film structures can be used as Schottky diodes.

EXPERIMENTAL

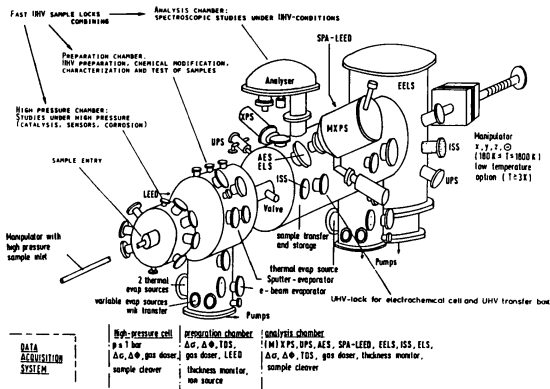
Lead phthalocyanine was purified in a carrier gas (N_2 and Ar) sublimation apparatus in a temperature gradient (300 K in 500 mm). Thin films were prepared under UHV conditions using a Knudsen cell with a liquid nitrogen cooling shield. The film thickness was measured with a quartz-crystal monitor (Edwards FTM4). The thickness of the thin films was determined spectroscopically from the decrease of a substrate XPS

(Mg $K\alpha$) signal by taking into consideration the mean free path of the different elements and kinetic energies involved. The optimum evaporation temperature in the Knudsen cell was 360 °C. At temperatures above 400 °C, partial decomposition of the phthalocyanines was observed.¹⁶ The substrate temperature during thin-film deposition was kept at 25 °C.

The Al_2O_3 and AgI substrates were sputtered and subsequently annealed to restore the ideal stoichiometry. The metal substrates Au, Pt and Cu were used as thin foils which, after sputtering and annealing, also showed negligible impurity contributions as tested by XPS and Auger Electron Spectroscopy (AES).

Substrate and thin-film preparations and most of the spectroscopic measurements were carried out in the multi-method UHV system shown schematically in Fig. 3a, with the different sample holders and transfer box to introduce or move the samples to other spectrometers as shown in Fig. 3b. The samples were introduced into the chamber in Fig. 3a on a substrate holder mounted on a solid transfer rod. The setup allowed heating and cooling between 80 and 1500 K. Locked in the rod, after its introduction in ambient air the sample passed through several differential pumping stations before reaching the high-pressure vessel ($p = 10^{-8}$ –1000 mbar) and the preparation and analysis vessels ($p \leq 10^{-10}$ mbar). This system makes possible the controlled exposure of the samples to high pressures of oxygen, water and/or synthetic air for subsequent gas-sensor testing. The separate UHV transfer system (Fig. 3b) makes possible the transfer of samples to separate UHV systems with scanning Auger (SAM) and EDX microscopes, secondary-ion mass (SIMS) and fast-atom bombardment (FAB-SIMS) spectroscopy facilities¹⁹ and another separate setup for FTIR spectroscopy.

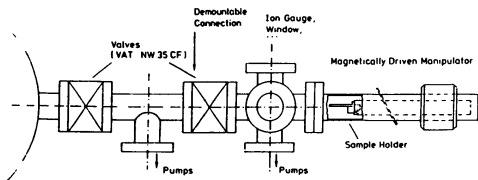
XPS was carried out with a magnesium $K\alpha$ source (LH, RQ10) at $h\nu = 1253.6$ eV. For UPS, a helium gas-discharge lamp (LH, UVS-10/35) was used. The HREELS (LH ELS 22) system was operated with an energy resolution of typically 10 meV at primary energies $E_0 = 5$ eV under specularly reflecting conditions with an angle of 60°. For the FTIR measurements (Bruker IFS 48 FTIR spectrometer operated with a resolution of 0.5 cm^{-1}) we used an MCT detector. Spectra were recorded either in transmission (NaCl, KBr, AgI) or in reflection (Al_2O_3 , Ag, Cu, Au, Pt) with an incident angle of 60°.



UHV Analysis Chambers

Sample Transfer Box

UHV Preparation Chambers

Sample Holder 1 (VSW / ϕ)

Sample Holder 2 (LH)

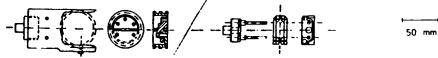


Figure 3. Schematic view of the experimental setup (top), sample transfer box (middle), and sample holders (bottom).

RESULTS AND DISCUSSION

X-ray photoemission spectroscopic (XPS) studies

XPS was used to control the cleaning procedures and to determine the elemental composition of substrate and thin-film structures. Typical results obtained for a PbPc thick film ($d = 4$ nm) are shown in Fig. 4. The characteristic C 1s splitting corresponds to different chemical bonds in the conjugated π -system (compare Fig. 2). The binding energies of the central Pb atoms are characteristic of Pb^{2+} ions. The intensity ratios of the C 1s relative to N 1s and Pb 4f levels are 1.8 and 1.3 and that of the N 1s relative to the Pb 4f level is 0.7. These ratios indicate stoichiometric films of ideal composition.¹⁶ For films prepared under UHV conditions, there is no emission in the O 1s region, indicating that the film is free from contamination. The XPS data for our films are in excellent agreement with earlier spectroscopic data.²⁰

In the following, we discuss the influence of oxygen on the stability of UHV-prepared PbPc and RuPc films.

PbPc films prepared under UHV conditions showed no reaction on exposure to oxygen at room temperature, as shown in Fig. 5 (*in situ* curve a). On the other hand, films prepared *ex situ* and transported in air show O 1s emission at 531.6 eV indicative of negatively charged OH groups (curve c). Slight annealing to 440 K causes a reduction in the emission at 531.6 eV, indicating that the OH-derived groups can be partially desorbed by heating.

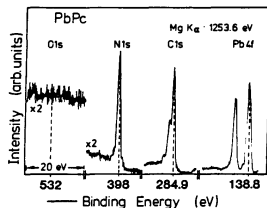


Figure 4. Characteristic XPS core level spectra of PbPc thick films (4 nm).

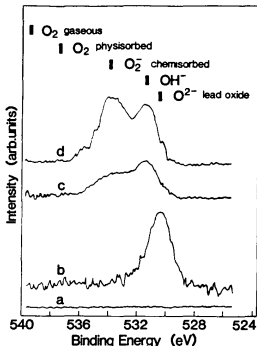


Figure 5. XPS (Mg K α) spectra of thick lead phthalocyanine films (4 nm) in the O 1s range prepared under UHV conditions *in situ* (a), after subsequent heating in 300 mbar of O₂ at 423 K (b), after exposing UHV-prepared films to ambient air (*ex situ*, c), and after subsequent heating in 300 mbar of O₂ at 423 K (d). Also indicated are characteristic binding energies of oxygen-related species.

All samples exposed to air have an additional emission at 534 eV (curves c and d). This emission increases on oxygen treatment at elevated temperatures. From the bars shown in the upper part of Fig. 5 we deduce that the binding energy of this species is relatively high and close to the value for oxygen molecules in the gas phase²¹ or in the physisorbed state.²² We therefore assign this emission to arise from O₂⁻. The broad emission in the O 1s range indicates the existence of two species, one OH-derived and an additional O₂-derived species.

Drastic changes are observed in the O 1s region after heating UHV-prepared thin films in pure oxygen at temperatures above 400 K (Fig. 5b). Under these conditions, Pb⁴⁺ is observed in the Pb 4f spectra. The O 1s signal at 529.6 eV is characteristic of oxides. Both signals indicate the formation of lead oxide, PbO_x. The formation of this oxide can be avoided in the presence of small amounts of water, e.g. by exposing UHV-prepared thin films to ambient air (Fig. 5c). Here, oxygen treatment at 150 °C and 100 mbar O₂

causes an increase in the O_{2s} emission at 534 eV. This preparation is required to obtain reproducible thin-film conductivity results (which is a prerequisite for the use of PbPc thin films as NO_2 or O_2 gas sensors). Figure 5d indicates that as-prepared 'water stabilized' thin films do not contain lead oxide. These films are capable of absorbing H_2O and O_2 reversibly with the interaction depending on the partial pressures and temperature and drastically changing the bulk conductivity,¹⁸ in agreement with earlier studies.²³ Oxygen adsorption and migration into the bulk have also been found for CoPc using Auger spectroscopy.²⁴

Amongst all the phthalocyanines, RuPc shows the highest conductivity at room temperature under ambient air conditions. Its application for hybrid devices and sensors therefore seemed of particular interest. However, we never found reversible changes in the conductivity when thin films were exposed to oxygen, although the initial conductivity of the thin films is very high even under UHV conditions. To explain these unusual findings, typical spectra of a RuPc film prepared and investigated under UHV *in situ* conditions are shown in Fig. 6 with their O 1s, N 1s, C 1s and Ru 3d levels. From the relative XPS intensities of the Ru 3d and C 1s levels we deduce that the com-

position of the sublimed layers is not stoichiometric, as the Ru 3d contribution is only 10% of that expected for ideal RuPc thin films. This finding is qualitatively the same for *ex situ* prepared thin films.

In Fig. 6, typical results are also shown for the interaction of RuPc with oxygen. Even films prepared *in situ* (Fig. 6a) usually have a significant O 1s contribution, which probably results from the RuPc evaporation material which contains small amounts of RuO_x surface oxides during the first evaporation cycle. In the preparation of oxygen-free ideal RuPc thin-film structures, extreme care therefore has to be taken to start from oxygen-free evaporation material. The gross elemental composition of the evaporation material, however, as determined by atomic absorption spectrometry, showed the ideal composition expected for RuPc. We therefore conclude that RuPc is covered with RuO_x , which forms a highly conducting thin surface layer during the interaction of RuPc with oxygen in the ambient air. The spectra in Fig. 6b were taken after treatment in pure O_2 (60 min at 370 K and 200 mbar). From the shift of the Ru 3d signals towards higher binding energies we deduce that Ru reacts with oxygen to form RuO_2 . For clarity the Ru 3d levels are shown separately in Fig. 7. Spectrum (a) is that of an *in situ* prepared thick film and spectrum (b) was obtained after heating that film in oxygen (100 mbar) at 400 K. The relative intensities of the Ru 3d and C 1s levels change significantly. Spectrum (c) was observed after heating the oxidized film at 400 K under vacuum. There is almost no emission remaining from C 1s and N 1s. Obviously, heating causes the RuO_2 layer to decompose into elemental Ru and oxygen.

The XPS data give clear evidence that RuPc films are not stable under ambient air conditions, but are always contaminated at the surface by RuO_2 . In contrast to PbPc, RuPc always forms surface oxides on exposure to oxygen and/or water. Ruthenium oxides form a highly conducting overlayer on RuPc thin films and also protect the inner RuPc from exchanging oxygen with the gas phase. Consequently, these exchange reactions, which are well known to lead to drastic conductivity changes for many phthalocyanines, are not observed for RuPc. Evidently, the conductivity values of RuPc measured under non-UHV conditions do not characterize intrinsic conduction behaviour. Therefore, a RuPc thin film does not show thermodynamically reversible controlled

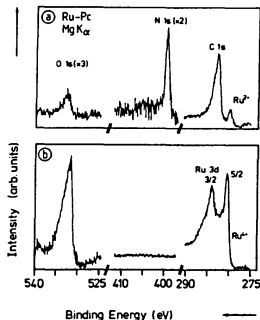


Figure 6. XPS spectra (O 1s, N 1s, C 1s and Ru 3d levels) of RuPc (5 nm) after UHV preparation (a) and after exposure to oxygen (300 mbar, 400 K) (b).

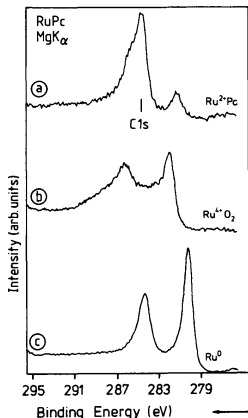


Figure 7. XPS spectra (Ru 3d) of RuPc (5 nm) after UHV preparation (a), after exposure to oxygen (300 mbar, 400 K) (b) and after annealing under UHV conditions at 400 K (c).

reactions with oxygen. This explains the irreversibility observed in the conductivity measurements of UHV-prepared thin films.

So far, we have discussed typical stabilities and chemical reactions at the interface between the organic layer and the gas phase (interface 1). We have focused on results obtained for thick films, which are not affected by film/substrate interactions (interface 2). These effects will now be discussed.

In a series of thin-film deposition experiments we observed that the XPS relative intensity ratios vary with increasing film thickness. Typical results are shown in Fig. 8 with characteristic XPS intensity ratios for PbPc thin films deposited on Pt and Ag substrates as a function of film thickness. The relative intensities at low coverages deviate significantly from the values for thick films. We have utilized these results as a fingerprint method to determine the reactivity of PbPc with different substrates at low film thicknesses. The examples in

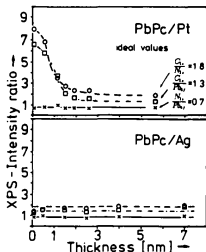


Figure 8. XPS intensity ratios of the C 1s, N 1s and Pb 4f core levels of PbPc as a function of film thickness for PbPc films evaporated on to Pt and Ag substrates.

Fig. 8 characterize a large amount of systematic data obtained for the other 'prototype' substrates, with the general result that XPS intensity ratios give easy access to the determination of conditions for non-ideal stoichiometry, i.e. for the formation of fragments in thin organic films. The data in Fig. 8 indicate that the interaction of PbPc with spectroscopically clean surfaces leads to deviations from stoichiometric values, particularly at low thicknesses. Similar experiments were performed on Al_2O_3 , AgI, Au, Pt, Ag and Cu surfaces.

To summarize the results, we observe stable stoichiometric films without decomposition products on Ag (Fig. 8), Au, SiO_2 , Al_2O_3 and AgI, and instability and decomposition products on Cu, Si and Pt surfaces (Fig. 8). Details of the interactions of Si and SiO_2 substrates with PbPc will be discussed in a separate paper.²⁵

Ultraviolet photoemission spectroscopic (UPS) studies

The electronic structure in the valence band is of principal interest in discussing the stability of film/substrate interfaces on the basis of molecular orbitals involved in the local bonding. A typical spectrum of the valence band range of a stoichiometric PbPc film is shown in Fig. 9. To a first approximation, the different peaks may be identified by the π -systems of the isoindole

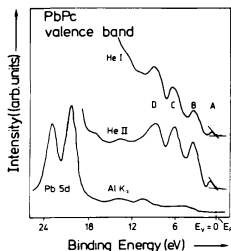


Figure 9. UPS and XPS spectra in the valence band range for PbPc thick films. For identification of peak positions, see Fig. 2 and Ref. 26.

moieties (A) and by the similarity to the molecular orbitals of the benzene molecule (B, C, D)²⁶ (see also Fig. 2).

Significant changes in the UPS valence band spectra are observed for those substrates for which independent XPS data show the formation of fragments. A detailed analysis, however, is extremely difficult because of several different possibilities of forming corresponding electronic states from different fragments.

More detailed and direct information about local bonding involving fragments at the interfaces may, however, be obtained from vibrational spectroscopy such as FTIR, integrating the dynamic structure behaviour over the whole film thickness, and from HREELS, giving information about dynamic structures in the first monolayer. Characteristic results from these techniques will now be discussed.

Fourier transform infrared (FTIR) spectroscopic studies

XPS spectra have been used to characterize conditions for forming films without or with decomposition at the interface. In the following sections we discuss the use of results from vibrational spectroscopy to characterize possible fragmentation processes and to identify fragments for the same systems. For FTIR measurements, the samples had to be transferred through air. In a first ap-

proximation to identify the dynamic structures, a reference spectrum was taken on NaCl (110) single crystals in transmission and the characteristic frequencies observed for such films are listed in Table 1. A comparison with data from the literature²⁷⁻³² shows that the most prominent features are in excellent agreement with the bands given in Table 1. The significant vibrations are marked by numbers with increasing wavenumbers of the corresponding vibrational mode. We consider frequencies that are almost unaffected by the structure of the macrocycle and which are characteristic of the local bonding within the molecule. The Pb-N vibration and normal modes of the macrocycle are too low to be detected with our spectrometer. Characteristic absorption bands are observed for the C-H vibration (1) at 720 cm^{-1} , the C-C vibrations of the benzene ring (2) at 1000 cm^{-1} , that of the pyrrole ring (3, 4) at 1280 and 1329 cm^{-1} , the C-N stretching mode of the pyrrole ring (5) at 1403 cm^{-1} , that of the aza bridges (6) at 1490 cm^{-1} and the C-C vibrations of the benzene ring (7) at 1586 and 1608 cm^{-1} . The aromatic C-H stretching vibrations (8) are observed at 3030 and 3050 cm^{-1} .

Table 1. Eigenfrequencies of phthalocyanine as determined from transmission FTIR of PbPc films sublimed on NaCl (110) crystals and assignment by data from the literature²⁷⁻³²

No.	Vibrational mode	cm^{-1}	meV
8	Arom. CH stretching	3050	378
		3030	376
7	CC stretching, benzene	1608	199
		1586	197
		1490	185
6	CN stretching, pyrrole	1479	183
		1403	174
5	CC stretching, pyrrole	1329	165
		1280	158
3	Ch bending	1156	143
		1114	138
		1078	134
2	CN bending	1058	131
		1000	124
		948	118
Modification	CN bending	883	109
		870	108
		815	101
Modification, macrocycle	CH bending	768	95
		740	92
		720	89
1	CH bending	643	80

For the following discussion we concentrate on the range between 1200 and 1800 cm^{-1} , which contains the vibrational modes labelled 3–7, as these are particularly sensitive to structural changes.

Typical FTIR results for PbPc thin films (thickness $d = 10$ nm) on metallic substrates are shown in Fig. 10a for the substrates Au, Cu and Pt. The spectra are normalized to the same absorbance. Even for these very thin films we find the typical ideal absorption frequencies on Cu

substrates listed in Table 1 without significant shifts or changes in the relative intensities. However, after annealing for several hours at temperatures around 450 K we observe a decrease of band 4 at 1403 cm^{-1} . Simultaneously, a new band at 1428 cm^{-1} shows up that is typical of CuPc.³³ The C–N vibration of the pyrrole ring characterizes the metal–macromolecule interaction, the shift of 25 cm^{-1} indicating substitution of the Pb central atom by Cu. This substitution is observed not only for extremely thin films but also for films with thicknesses of the order of 100 nm. This observation of exchanging central atoms is in line with the mass spectrometric data: we identified CuPc in a molecular beam of PbPc after its interaction with hot Cu surfaces.

The spectra obtained for PbPc on Pt show negligible fine structure below a film thickness of 20 nm with an absorption only observable around 700 cm^{-1} in the CH bending mode region. Thicker films show the typical PbPc vibrations listed in Table 1. The lack of any resolvable structure is an indication of fragmentation. The lack of any absorption in the frequency range 1000–1700 cm^{-1} is a clear indication that no aromatic fragments are present.

The corresponding spectra obtained for PcPc on Au are different (top spectrum in Fig. 10a). The main absorption frequencies are still observable. The C–C stretching vibration mode of the pyrrole ring (3), however, is strongly enhanced and the vibrational bands of the C–N stretching vibration (5, 6) are shifted to lower frequencies. In addition, we find a strong absorption band around 1745 cm^{-1} , a frequency range characteristic of CO stretching vibrations. Further, we find strong absorption in the CH vibration range below 3000 cm^{-1} (Fig. 10b), which we identify as arising from aliphatic fragments. The intensity of these bands is reduced when thick PbPc films are investigated.

The data in Fig. 10 indicate substantial differences for the different substrates. For Cu, the vibrational spectra are almost unperturbed, indicating that the Pc molecules remain unaffected even in the submonolayer range. The central Pb atom in the ring, however, is exchanged by Cu (see above). For Pt, the lack of any structured absorption band is indicative of dissociative interaction. This is in agreement with the XPS data presented earlier. For Au, the changes in the pyrrole-derived bands and the strong CO band clearly show that the macrocycle is oxidized during transfer of the

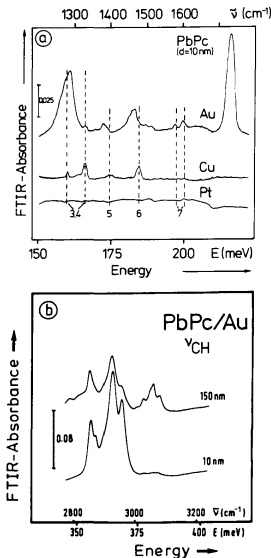


Figure 10. (a) FTIR absorption spectra of PbPc films (film thickness $d = 10$ nm) on Au, Cu and Pt substrates after exposure to air. (b) FTIR absorption spectra in the CH stretch vibration range for two different films ($d = 10$ and 150 nm) on Au substrates after exposure to air.

sample through air. Films not exposed to air show XPS intensity ratios characteristic of unaffected Pc molecules. From the strong aliphatic bands and the frequency of the C–O vibration which corresponds to that of acetone, we conclude that the benzene ring system has lost its aromaticity during catalytic oxidation at the interface. At greater film thickness, the increasing intensity of the aromatic CH band indicates that the influence of the Au-derived catalytic oxidation is now reduced.

High-resolution electron energy loss spectroscopic (HREELS) studies

We also performed HREELS studies in order to identify fragments of the organic molecules at the inorganic interfaces in the (sub-)monolayer range. Although details of the physics of this technique when applied to surfaces of large organic molecules need some further clarification,³⁴ a direct comparison of vibrational data obtained in HREELS and in FTIR measurements yields information about fragmentation in the submonolayer range. Better energy resolution is evidently obtained by FTIR than HREELS. The information depth, however, is far smaller in HREELS. This makes it possible to identify dynamic structures in the top-most layer of the films, whereas in FTIR the integrated information exceeds the film thickness of all the films investigated in this study.

As a typical example, Fig. 11 shows the thickness dependence of the HREELS data for PbPc on a Pt foil. For comparison, the characteristic vibrational modes of chemically perfect films observed in FTIR are also indicated (compare also Table 1). This sequence demonstrates that small changes in the HREELS data are observable, except at very low coverages of PbPc. In the submonolayer range of PbPc on Pt in particular, the losses around 90 meV are dominant, whereas those around 180 meV (1400 cm^{-1}) are absent. At higher coverages, there are three groups in that range, peaking at around 90, 120 and 180 meV. The assignment of these losses can be made by direct comparison with the FTIR data presented in Table 1 and Fig. 10. These losses arise from excitation of the C–H bending mode (1), the C–C stretching vibrations of benzene (2) and pyrrole (3, 4) and the C–N stretching vibrations of pyrrole (5) and of the aza bridges (6).

For submonolayer coverages of PbPc on Pt

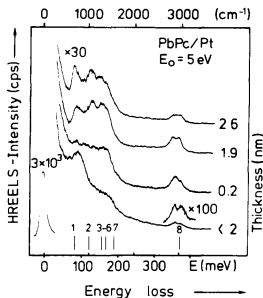


Figure 11. Characteristic HREELS spectra of PbPc thin films on Pt substrates for different film thicknesses between 0.1 and 2.6 nm.

foils, the absence of the CN-derived excitations indicates a fragmentation of these molecules probably around the pyrrole structure or the aza groups. This possible explanation is supported by XPS results that indicate a lack of N and Pb under the same conditions.

Typical HREELS results for PbPc thin films in the submonolayer range at Au, Cu and Pt substrates are shown in Fig. 12. As a general result, we observe that the intensity of the elastic peak is very low, particularly for higher coverages of thin films. The characteristic losses are well resolved and appear as strong signals. We observe the aromatic CH stretching modes ($\nu > 3000 \text{ cm}^{-1}$), the CH bending modes (around 1000 cm^{-1}) and weak contributions only from the C–N vibration (around 1400 cm^{-1}). These losses are in good agreement with the main absorption bands observed in the FTIR spectra.

A further general result is the occurrence of CH stretching frequencies below 360 meV almost independent of the coverage of the organic overlayer. Frequencies in that range are usually assigned to aliphatic CH stretching frequencies. However, we do not observe a systematic trend in the dynamic structure of stable films that would show up in the aromatic range, or of dissociated molecules with contributions that would show up in the aliphatic range at low coverages. We therefore conclude that the observed losses result

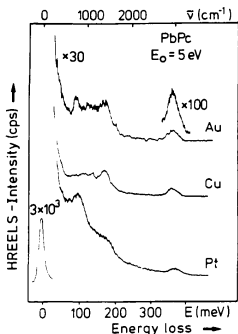


Figure 12. Characteristic HREELS spectra of PbPc for the different substrates Au, Cu and Pt (film thickness $d < 0.2$ nm).

from different scattering mechanisms of the two different possible CH vibrations that allow a selective excitation of fragments.

CONCLUSIONS

The high thermal stability of metal phthalocyanines and the possibility of a systematic variation of their chemical, electrical and optical properties by exchanging their central atoms or by substituting their organic ligands makes this class of material particularly suitable for both, theoretical studies and practical applications. The prerequisite in both instances, however, is reproducibility in preparing ideal film structures. This requires that uncontrolled molecular fragments can be avoided at the interfaces between the thin films and the gas phase (interface 1) and thin films and the substrates (interface 2).

Indications of the formation of fragments can be deduced from modified XPS intensity ratios of the different elements in the phthalocyanines, from modified vibrational spectra, and from modified FAB-SIMS spectra.²⁵

Our results indicate that the thin film/gas bound

dary (interface 1) is extremely unstable for RuPc thin films. PbPc, however, shows stable surfaces and reversible concentration changes of adsorbed and adsorbed species under atmospheric pressure conditions as checked, e.g., by changes in the conductivity when exposed to oxygen or water. Bulk doping of O_2^- on exposure to oxygen increases intrinsic conductivities by orders of magnitudes.¹⁸ The formation of RuO_x at the surface cannot be avoided under atmospheric pressure conditions. This oxide surface layer protects the underlying RuPc from the ambient air and has a high conductivity. These layers cannot be removed, either thermally or by sputtering or any other chemical treatment. The interface between metal phthalocyanines and oxygen generally tends to form central atom (Pb or Ru) oxides. The formation of PbO_x can be avoided in the presence of small amounts of water. The presence of RuO_x can never be avoided during exposure to oxygen.

The influence of the substrate (interface 2) on the organic overlayers is characterized by the existence or non-existence of organic fragments. The latter can be avoided if ionic substrates such as Al_2O_3 or AgI are used. These substrates show negligible electronic contributions from surface bonds in the band gap and offer energetically low-lying valence-band states which do not couple with the corresponding molecular orbital states in the phthalocyanines.

A detailed characterization of Pc fragments formed at the reactive substrates in the submonolayer range is difficult. The following characteristic reactions however, could be identified for PbPc thin film/substrate interactions: first, we deduce an exchange of the PbPc central atom (Pb) with substrate atoms (Cu) from mass spectrometric, FAB-SIMS and FTIR data; second, we deduce that the pyrrole ring is unstable at Pt and Au substrates from FTIR and HREELS vibrational spectra; third, we deduce that the benzene ring is stable at the substrates Au and Pt, as the C-C stretching vibrations of benzene appear with no significant shift; we observe a decomposition of PbPc at gold surfaces after exposure to air.

In conclusion, the results indicate that the reactivity of phthalocyanine thin films with both the substrate and the gas phase is far more pronounced than has been assumed in the past. This may be the reason why a wide variety of different inconsistent results have been published concerning, e.g., the sensor properties, optical behaviour,

conductivities and catalytic activities of phthalocyanine thin-film structures. We have determined conditions under which these structures can be reproduced. This is a prerequisite for further systematic studies in the fields of molecular electronics and sensors.

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