A study of the Ni-Phthalocyanine / gold interface using X-Ray and ultraviolet photoelectron spectroscopies

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Abstract. Nickel Phthalocyanine (NiPc) thin films (~25nm thick) were grown stepwise on a polycrystalline Au substrate and the interface was characterized by X-Ray and Ultraviolet Photoelectron Spectroscopies (XPS, UPS). The C1s peak of the bulk (~5 nm) NiPc film was resolved into three components reflecting photoemission from multiple sites within the molecule. The peak at 284.8 eV corresponds to C-C bonds, the one at 286.2 eV to C–N bonds, while the last one at 287.9 eV is satellite of the main peak. The Ni 2p and N1s peaks appear at ~855.9 eV and ~399.3 eV respectively and are due to Ni-N bonds. The NiPc Highest Occupied Molecular Orbital (HOMO) cut-off position was determined from the valence band spectrum of the bulk organic film, and was found at ~1.00 eV from the analyser Fermi level. The work function of the Au foil and the bulk NiPc film were found to be 5.20 ± 0.05 eV and 4.20 ± 0.05 eV respectively. The combination of UPS and XPS results led to the determination of the energy level diagram of the NiPc/Au interface.

1. Introduction
In recent years semiconducting organic materials have received increasing attention due to their successful application in optical and electronic devices. Phthalocyanines (Pcs) is a versatile class of medium sized organic molecules. These materials are already widely used in gas sensor technology and in electronic devices [1] because of their advantageous properties such as thermal, chemical and photochemical stability, excellent film growth and optimised optical and electronic properties. The knowledge of barrier heights at interfaces between the electrodes and the active organic layers is of enormous importance for understanding and improvement of organic semiconductor devices.

In this work we investigate the interface formed by depositing Nickel Phthalocyanine (NiPc) on polycrystalline gold using XP and UP Spectroscopies. NiPc is an organic semiconductor with a relatively high mobility value (~1×10⁻⁵ m² V⁻¹ s⁻¹) as compared to other Pc compounds [2-4], which makes it a promising candidate for development of future electronic devices. The metallic gold substrate was chosen because it has high work function and it forms abrupt interfaces with Pcs[5-9]. It is also widely used as an electrode material in organic devices.

2. Experimental
The experiments were carried out in a multichamber UHV system [10] (base pressure ~2×10⁻¹⁰ mbar) which allows the preparation of interfaces with high purity and controlled thickness. The characterization of the interfaces was done with XPS and UPS. The XPS measurements were obtained
with unmonochromatic AlKα source at 1486.6 eV and an analyser pass energy of 97 eV while for UPS the HeI (21.2 eV) radiation was used. The spectrometer was calibrated by the Au4f7/2 core level (84.1 eV) for clean Au. During UPS measurements a −12.28 V bias was applied to the sample in order to separate sample and analyzer high binding energy cutoffs. The polycrystalline Au foil was cleaned by Ar⁺ sputtering and annealing at 400 °C. Commercial NiPc powder from Alfa Aesar was evaporated from a home-made deposition source [11] Thin films of NiPc were produced in situ by evaporation in a step wise manner on the clean Au substrate. During evaporation, NiPc evaporation cell was heated at 425 °C and the pressure was less than 5×10⁻⁸ mbar. After every deposition step the surface of the sample was characterized by XPS and UPS. The film thickness was estimated using XPS by the attenuation of the intensity of the substrate peak (Au4f) due to the NiPc overlayer (C1s) assuming a layer by layer growth mode for small coverages [12, 13].

3. Results and discussion

Figure 1 presents the variation of C1s peak of the NiPc/Au interface for different organic film thicknesses. All the XPS core level peaks were fitted with Lorentzian and Gaussian functions after the subtraction of a Shirley-type background [14].

The C1s peak attributed to NiPc appears after the first deposition and its intensity increases as the organic film grows thicker. The C1s peak for the organic film was resolved into three components, reflecting photoemission from multiple sites within the molecule (figure 2). The final position of XPS C1s components for the bulk organic overlayer are 284.8 eV which corresponds to the aromatic carbon of benzene rings, 286.2 eV to pyrrole carbon linked to nitrogen [15,16] and 287.9 eV which can be attributed to satellite of the main peak[7,17]. The observed intensity ratio C-C/C-N is 1/0.33 in agreement with the number of C–C and C–N bonds in the NiPc molecule. There is a total shift of 0.6 eV of the C1s peak toward higher energies with increasing organic layer thickness. The position and FWHM of Au4f peak remains stable, while its intensity gradually attenuates upon deposition. No O1s peak was detected. The absence of additional components in XPS C1s and Au4f (not shown) core levels at submonolayer coverages indicates that the formed interface is abrupt without chemical interactions or possible interfacial states.

Figure 1. Variation of C1s of the interface NiPc/Au during deposition.

Figure 2. Analysis of the XPS C1s peak for an organic film of 5 nm thick.

Figure 3. XPS BE shio1s versus NiPc thickness.
The XPS N1s peak of the organic film has lower intensity than the C1s peak because of the atomic ratio N/C (≈8/32) in the NiPc molecule. The N1s peak of the bulk NiPc film (5nm) appears at 399.3 eV with FWHM=1.85 eV and Ni2p3/2 at 855.9 eV. Figure 3 shows the XPS BE shift of C1s with increasing NiPc thickness. Figure 4 presents the change of the UP spectra of NiPc/Au interface in various organic film thickness up to 25 nm. The bottom spectrum shows the clean Au substrate and is composed of Au5d orbitals. The metal Fermi cutoff is clearly visible. For submonolayer coverage new features appear and, as the coverage increases, those of Au5d are gradually attenuated. At a film thickness of about 2.5 nm NiPc specific characteristics have fully developed and those of the substrate are completely covered which suggests a layer by layer growth mode [18]. The analyzer resolution is determined from the width of the Au Fermi edge and it is 0.16 eV.

The work function of the clean Au substrate was specified to be 5.20±0.05 eV in agreement with literature [19]. There is a total decrease of the work function of 1.00 eV during depositions and finally the work function of the NiPc overlayer is found 4.20±0.05 eV. Figure 4 shows the valence band of the NiPc/Au interface. The full spectra are shown in the center part. On the left, the high binding energy cutoff region of the spectra are shown normalized, to allow better comparison. On the right, the development of the HOMO peak with increasing organic thickness is shown.

The HOMO cutoff of the bulk NiPc film is at 1.00±0.05 eV for a coverage of 5 nm. The valence band structure of the bulk NiPc overlayer (5 nm) is composed of four peaks at BE’s: 1.50 eV, 3.80 eV, 6.60 eV and 8.85 eV. The density of the upper UV-spectra in the 6 to 12 eV range is attributed to orbitals from benzene and pyrrole, which are common to all Pc molecules. Substitution of one metal atom has only minor influence on the electronic structure of the upper valence bands [20]. The valence band structures between 0 and 6 eV correspond to the d-electron state of the central metal atom and results from the interaction of metal d-electrons with the four central N atoms, in agreement with theoretical calculations of NiPc valence band [20-24].

As it is not possible to determine exactly the energetic shift in the UPS spectra, because it is superimposed by the large density of states of the metallic substrate and the variation of the HOMO as a function of the coverage, we combine UPS and XPS measurements in order to get valuable information for the NiPc/Au interface. According to Figure 3 we observe a ~0.45 eV shift of C1s XPS peak for coverages up to 2.0 nm towards higher binding energies which is attributed to screening effects [5,25,26]. For thicker NiPc films the observed shift is about 0.15 eV and is due to band bending, as at these large coverages the presence of screening effects is negligible. Therefore, from XPS data the total band bending is \( V_b = 0.15 \) eV while from UV spectra, as we showed previously, the total work function change is \( \Delta \Phi = 1.00 \pm 0.05 \) eV. Thus, the interface dipole \( \phi_D = \Delta \Phi - V_b = (1.00 - 0.15) \) eV≈ 0.85 eV. The formed interface is not reactive and the interface dipole...
indicates the transfer of negative charge from NiPc to Au due to the large work function change between the two materials. Ionization potential can be calculated by: \( I = \Phi_{(NiPc)} + \text{HOMO cutoff} = (4.20 + 1.00) \text{ eV} = 5.20 \text{ eV} \), in agreement with literature for other Pc compounds\[27\]. In order to determine the barrier \( \Phi_{bh} \) between the Au Fermi level and HOMO cutoff of the thick NiPc overlayer, it is necessary to calculate the offset between them. Since the Fermi level is defined to be zero, the hole injection barrier (\( \Phi_{bh} \)) at the interface is determined from the UPS spectrum at a coverage of 5 nm by: \( \Phi_{bh} = \text{HOMO cutoff} - V_b = (1.00 \pm 0.15) \text{ eV} = 0.85 \text{ eV} \). The energy difference between HOMO and LUMO according to electronic structure calculations\[23\], since the unoccupied LUMO states are not accessible by photoemission spectroscopy, is \( E_g = 2.41 \text{ eV} \). Thus, the electron injection barrier is \( \Phi_{be} = \Phi_{bh} - E_g = (0.85 - 2.41) \text{ eV} = -1.46 \text{ eV} \). Figure 5 represents the energy diagram of the NiPc/Au interface which is a result of the combination of XPS and UPS results.

4. Summary

The electronic structure of the NiPc/Au interface has been investigated using core and valence level photoemission spectroscopy. The observed total upward binding energy shift of 0.6 eV of the NiPc XPS core levels is attributed first to screening effects induced by the metallic substrate (0.45 eV) for organic film thickness up to 2.0 nm and to band bending (0.15 eV) at the organic overlayer. For a film thickness of 2.5 nm the NiPc valence band specific characteristics have fully developed and those of the substrate are completely covered. The HOMO cutoff of the NiPc film takes its final value, 1.00 \( \pm \) 0.05 eV, at a coverage of 5 nm in agreement with electronic structure calculations. The NiPc valence band is composed of four peaks at 1.50 eV, 3.80 eV, 6.60 eV and 8.85 eV of binding energy.

5. References

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