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## Hybrid organic spin valves

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## Energy level alignment symmetry at Co/pentacene/Co interfaces<sup>1</sup>

We have employed X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) to study the energy level alignment and energetics at the Co/pentacene/Co interfaces. In the case of pentacene deposition on Co we found an interfacial dipole of about 1.1 eV and a hole injection barrier of 1.0 eV, whereas for the case of Co deposition on pentacene we found a similar 1.0 eV value for the hole injection barrier and vacuum level alignment ( $\sim 0$  eV interfacial dipole), respectively. By combining XPS and UPS we were able to identify that hybridization occurs between pentacene and Co. The results of the deposition of the reactive Co on pentacene indicates only a small penetration depth of the metal atoms into the pentacene layer. A complete band diagram for the layered Co/pentacene/Co structure is presented in the frame of a rigid band model with interfacial dipoles. Finally, our findings are linked to spin injection experiments.

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## 4.1 Introduction

The nature of the Co/pentacene contact (ohmic, Schottky barrier) is of great importance for pentacene spin valve devices due to the conductivity mismatch problem (see *Chapter 2*). The Schottky-Mott rule of vacuum alignment, taking into account the very similar values of Co work function and ionization potential of pentacene ( $\sim 5.0$  eV), predicts an ohmic contact for the Co/pentacene interface. However, in general, this rule of vacuum alignment does not hold at organic/metal interfaces [1, 2]. The interfacial energy level alignment is described by the slope parameter  $S = -d\Delta_h/d\Phi_m$  where  $\Delta_h$  and  $\Phi_m$  represent the hole injection barrier and the metal work function. Literature reports on the energy level alignment at various metal/pentacene interfaces [3–8] indicate a slope parameter of  $-0.46$  in [7] and of  $-0.42$  in [8]. Taking  $\Phi_{Co} = 5.0$  eV (see later) and  $S = -0.42$ ,  $\Delta_h(Au) = 0.7$  eV,  $\Phi_{Au} = 5.3$  eV [8] we estimate a hole injection barrier of 0.8 eV for the Co/pentacene interface, in disagreement with our measurements of 1.0 eV. Given the properties of pristine Co and pentacene it is not possible to predict the nature of the contact, therefore the hole injection barrier has to be determined experimentally, from photoelectron spectroscopy [9, 10] or electrical measurements for example.

In this chapter we present the energy level alignment at Co/P (i.e. pentacene deposited on Co) and P/Co (i.e. Co deposited on pentacene) interfaces, studied by photoelectron spectroscopy experiments. By combining X-ray and ultraviolet photoelectron spectroscopy experiments (XPS and UPS) we accurately deduced the energy level alignment and the chemical activity at these interfaces. Due to the high reactivity of the Co metal, chemical reaction may be expected at these interfaces. In these experiments, pentacene (Co) is deposited in a sequential manner on Co (pentacene) and after each deposition step XPS and UPS spectra are recorded. The surface sensitivity of PES (few monolayers) enables the sampling of the electrostatic potential within pentacene as a function of its thickness atop of a Co thin film and provides clues about the energy level alignment mechanism at the interface and far from it. Moreover, a possible spin valve geometry is a layered structure in which pentacene is sandwiched between two Co electrodes. The deposition of metals on the loose organic matrix may be accompanied by diffusion of the metal atoms, leading to an ill defined interface which is very different from the sharp interface in which the organic is deposited on the metal. In consequence the barrier heights at the two interfaces may be different and the device current-voltage characteristics become asymmetric [1, 2, 11]. Therefore, it is of interest to study both interfaces and we will show that they provide complementary information on the interaction between Co and pentacene. The experimental conditions have been presented in *Section 3.3*.

## 4.2 Co/pentacene interface

In Fig. 4.1 we present UPS spectra of clean Co and of 30 Å pentacene deposited on Co with the energy scales in both binding energy (BE) and kinetic energy (KE). The spectra are characterized by two sharp cut-offs. The Fermi level (FL) cut-off at high kinetic energies represents electrons excited from FL. The secondary electron cut-off (SEC) at low kinetic energies is given by multiply inelastically scattered electrons which just reached the vacuum level (VL). Following the discussion presented in *Section 2.2.3*, by subtracting the width of the spectrum from the energy of the light we get a value of 5.0 eV for the Co work function (spectrometer broadening corrected). Additionally, the ionization potential (IP) of the pentacene layer is obtained in the same manner and amounts to 4.9 eV at 30 Å pentacene coverage. The distance between leading edge of the highest molecular orbital (HOMO) and FL represents the hole injection barrier ( $\Delta_h$ ), whereas the shift of SEC (i.e. VL) gives the magnitude of the interfacial dipole ( $\Delta$ ). Also shown in Fig. 4.1 are some deep lying levels of pentacene, which we denoted as "a" and "b".

In Fig. 4.2(a), (b) and (c), a close up of the SEC, HOMO and C 1s evolution for all pentacene thicknesses investigated, is shown. At the very first deposition step of 5 Å, we observe a sudden shift of the VL of about 0.9 eV. Up to 30 Å, that is  $\approx$

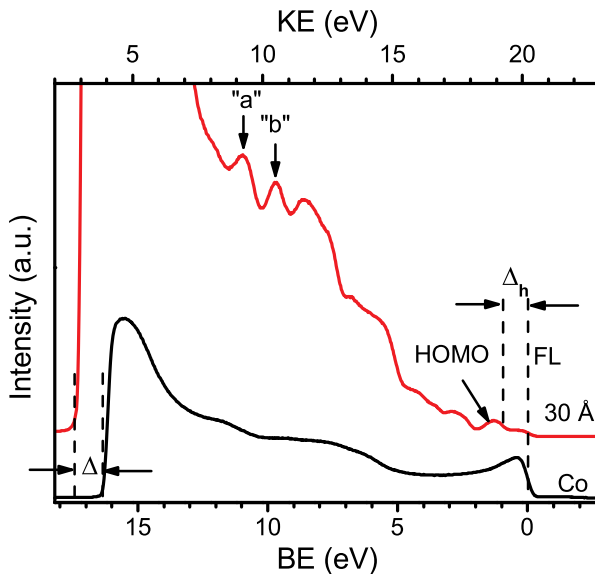


Figure 4.1: UPS spectra of clean Co and of 30 Å pentacene deposited on Co, see text for more explanations.

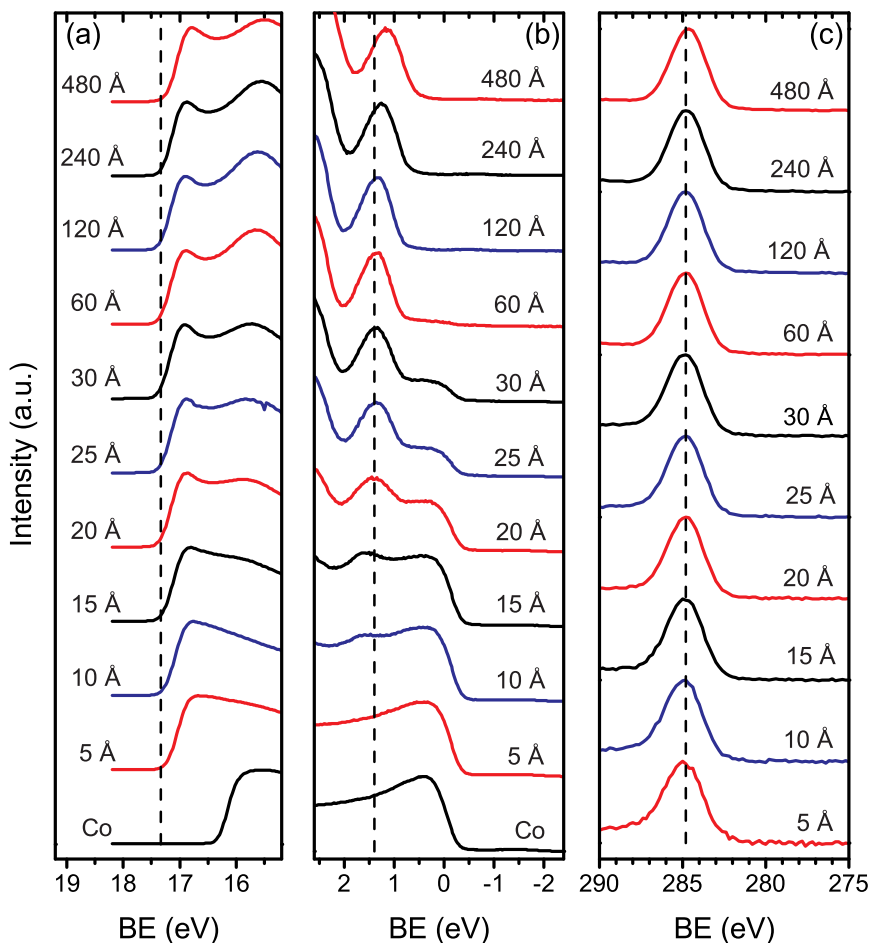


Figure 4.2: The evolution of the energy levels (normalized) with increasing pentacene thickness: a) secondary electron cut-off (SEC), b) HOMO level and c) C 1s energy level. The vertical dashed lines represent the values of SEC, HOMO and C 1s respectively at a thickness of 30 Å.

2 monolayers pentacene [12], the VL shift gradually increases and reaches a value of 1.1 eV. This shift of the VL corresponds to lowering of the work function of the sample. In the region near FL, at 5 Å pentacene the HOMO is not distinguishable but becomes visible at 10 Å. Up to 30 Å HOMO level shifts gradually to lower binding energies. Estimated at 30 Å, we found  $\Delta_h = 1.0$  eV and  $\Delta = 1.1$  eV. For pentacene coverage higher than 30 Å, VL, HOMO and C 1s follow approximately the same shift towards lower binding energies. Charging effects caused by removal of electrons from the sample can be excluded since the levels move towards lower

binding energies, i.e. higher kinetic energies.

The position of "a", "b", HOMO are extracted by fitting with single gaussian functions after a linear background subtraction, whereas C 1s was fitted using a single gaussian with Shirley background subtraction [13]. Their evolution, together with VL evolution is shown in Fig. 4.3 as a function of pentacene coverage. The energy shifts are expressed as the binding energy shift with respect to the value at 480 Å, i.e.  $BE(d) - BE(d = 480\text{Å})$ . Note that the binding energy shift scale is flipped, so that the energy levels shift resembles the schematic on Fig. 2.9. All energy levels follow the same trend with only small differences. The changes observed can be divided into two regimes: a *low coverage* regime for pentacene thicknesses up to 30 Å and a *high coverage* one from 30 to 480 Å. The intensity of the HOMO level and the attenuation of the spectral intensity at approximately the maximum of the Co 3d band position (denoted as FL intensity), saturate at a nominal thickness somewhere between 30 and 60 Å (2-4 monolayers), see the inset in Fig. 4.3. Saturation occurs when the pentacene layer becomes thick enough so that the substrate signals are not present in the spectra. Therefore, in the *low coverage* regime we are probing the *interfacial* properties whereas in the *high coverage* regime we probe the bulk like properties of pentacene. Next, we separately discuss phenomena that may be responsible for the energy level alignment in the two regimes.

### 4.2.1 The low coverage regime: the interfacial energy level alignment

The vacuum level evolution is determined by the contribution of several phenomena, such as interfacial dipole, charge transfer, chemical reaction, image potential, polarization effects and band bending. One widely encountered phenomenon at metal-organic interfaces is the work function modification of the metal by the first monolayer of organic molecules, known also as the "pillow effect" [1,2,14,15]. The electron cloud of the adsorbed pentacene molecules interacts with surface dipole of the metal substrate and compresses it, therefore the contribution of the surface dipole to the metal work function is partly removed [16–18]. This leads to the lowering of the work function and the result is an apparent interface dipole, which does not necessarily mean that an interfacial dipole is created but rather that the existent surface dipole is modified. The slight bending, up to 30 Å, shows an interfacial dipole which evolves gradually. This gradual shift of the vacuum level in the low coverage regime may be explained by the following. At the initial stages of growth the pentacene molecules nucleate at step edges or defects, exactly in the regions where the surface dipole contributes less to the total surface dipole. Therefore, the interaction with the metallic substrate is apparently less than in

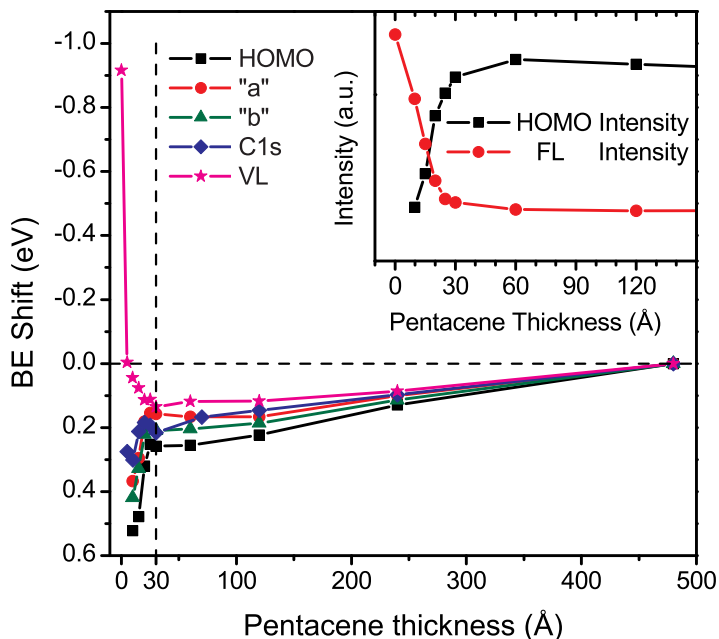


Figure 4.3: The binding energy shifts of the energy levels: HOMO, "a", "b", C 1s and VL, as a function of pentacene thickness. The BE shifts are expressed as  $BE(d) - BE(d = 480\text{\AA})$ , where  $d$  represents the pentacene thickness. Note the flipped BE scale. Two distinct regimes are observed: *low coverage* up to 30 Å, and *high coverage* for thicknesses higher than 30 Å.

the case of a 30 Å film situation. The random orientation of the molecules on the polycrystalline Co substrate may also lead to a smaller surface dipole. The substrate screening (the image potential) can play an important role as well, since the few dipoles created at the beginning of the growth will be screened by the free electrons from the Co metal. These effects lead to a total measured interfacial dipole smaller than in the case when most of the molecules have the same preferred orientation.

We now turn the attention to the FL-HOMO region of the spectra in this *interfacial* regime. The Co 3d band consists of orbitals which are very close in energy with respect to the HOMO of pentacene. Such a high degree of orbital overlap may induce hybridization or chemisorption of pentacene molecules on the Co surface. Formation of new bonds or hybridization leads to the modification of the energy levels near the interface and (very) likely to charge redistribution in

the interfacial layer. In the interfacial region the HOMO level is found at higher binding energies compared with a thick film situation. Moreover, at a coverage of 5 Å the HOMO level is not visible. These effects hint to a chemical reaction or hybridization which could lead to the formation of gap states. The high spectral intensity at the Fermi level due to Co 3d band hinders the clear observation of such states. In search for the evidence of these states one may perform a scaling of the clean Co spectrum and subtract it from the measured spectrum at 5 Å pentacene coverage. We do not perform such an operation, since the measured spectrum at 5 Å pentacene cannot be represented as a simple addition of the clean Co spectrum and the 5 Å pentacene spectrum. The inelastically scattered electrons originating from the Co 3d band (at the FL) gives rise to an increase in the background at binding energies corresponding to possible states in the band gap of pentacene. Therefore, the subtraction of the Co spectrum would presume spectral intensity in the pentacene band gap which has nothing to do with electronic states present in the band gap of pentacene. A significant contribution of the polarization energy and the image potential would shift the energy levels towards lower binding energies, which is not the case. It seems that hybridization gives a stronger and opposite effect.

Another cause for the observed high binding energy of the HOMO in the interfacial layer is the charge transfer due to chemical potential equilibration, i.e. band bending. For the purified pentacene the Fermi level is expected to be very close to the middle of the band gap. Given the ionization potential of pentacene of 4.9 eV (see previous) it is obvious that the FL of pentacene is higher in energy than the FL of Co with respect to a common VL. Therefore, FL alignment requires electrons to flow from pentacene to Co. This leads to a positively charged pentacene layer at the interface as compared with the situation far from the interface in agreement with the measurements. The possible contribution of this effect to the observed interfacial dipole has the same sign as the "pillow effect" and adds up.

### 4.2.2 The high coverage regime: the bulk pentacene energy level alignment

In Fig. 4.4 we present the C 1s energy level parameters, i.e. BE, full width at half maximum (FWHM) and intensity, extracted from a fit as function of pentacene coverage. The energetic disorder (expressed by the FWHM of the C 1s line) saturates around 60 Å, whereas the intensity shows signs of saturation somewhere around 120 Å. The saturation in the XPS spectra occurs later than in UPS spectra as expected and is due to different kinetic energies of photoelectrons of  $\approx 19$  eV in UPS vs.  $\approx 1000$  eV for C 1s in XPS, that is different mean free paths of the



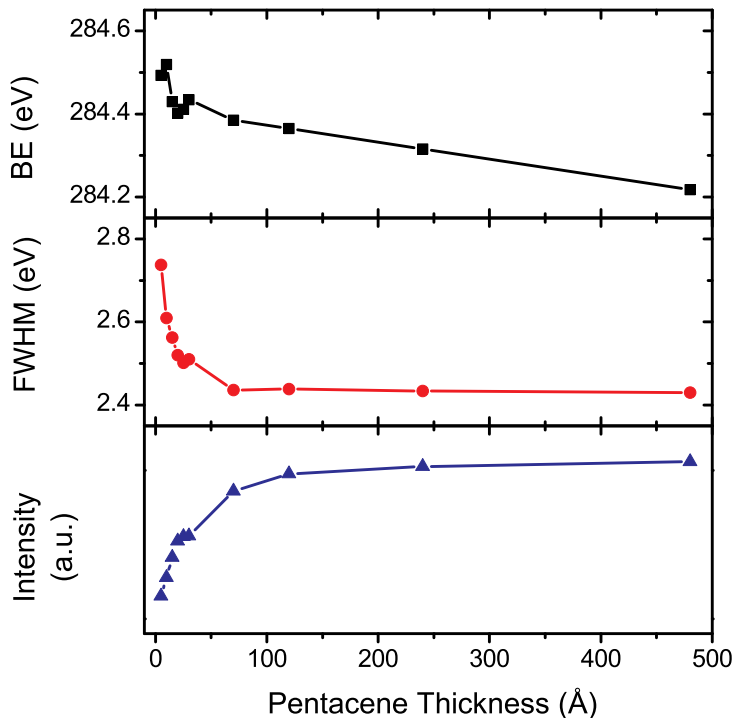


Figure 4.4: C 1s energy level parameters: binding energy (BE), full width half maximum (FWHM) and intensity as a function of pentacene coverage.

photoelectrons, fact which determines different probing depths in the two PES experiments. The saturation behavior of C 1s FWHM is consistent with the idea that the line broadening is due to different BE for the C 1s in the interfacial layer. We can conclude without doubt that most of the changes observed in the spectra are due to phenomena taking place at the *interfacial* layer. Therefore, XPS spectra at +60 Å is characteristic to the bulk properties of the pentacene film. Strictly speaking, if band bending phenomena are relevant for the energy level alignment we are probing the depletion region in this regime.

The BE of all energy levels, see Fig. 4.3, are higher for the interfacial layer compared with the thick film situation and all follow approximately the same shifts in this *high coverage regime*. This is consistent with a purely electrostatic effect and possible causes for the monotonous shift of the energy levels are the polarization energy, band bending and morphology changes. An increase in the polarization energy with the increase in the pentacene layer may be expected [19, 20]. This effect shifts the energy levels towards lower binding energies, in agreement with our observations. But, on the other hand, the energy levels shift due to polariza-

tion energy should show saturation behavior which is not the case for the range of thicknesses we investigated. In the purified, undoped, wide band gap pentacene film there are few free charge carriers available, therefore no significant band bending is expected for the range of thicknesses investigated, perhaps in agreement with only  $\sim 0.3$  eV difference between the HOMO at 30 Å and 480 Å respectively, and  $\sim 0.1$  eV between VLS in the same range of thicknesses.

### 4.3 Pentacene/Co interface

In this section we discuss the case of Co deposition on pentacene, the P/Co interface. Compared with the very sharp and well defined Co/P interface, the P/Co interface is more complex since metal atoms may diffuse in the pentacene layer. However, the study of P/Co interface can provide additional information in the interaction of pentacene with Co. For example, at very low Co coverages there is no metallic surface yet, but still chemical reactions going on. With the onset of the metallic behavior we turn on the metallic layer screening. We believe that the study of this interface brings complementary and valuable knowledge about the former well defined interface (Co/P). The experiments are done in the same manner as for the Co/P interface with the roles of Co and pentacene interchanged, that is Co is deposited sequentially on a pentacene film. We investigated this interface in 3 similar samples with Co as bottom metal layer ( $\sim 50$  to  $100$  Å) and  $\sim 480$  Å pentacene. Charging effects are excluded because the Fermi edge of the top deposited Co agrees with the one of the bottom Co.

The measured UPS spectra in the region of HOMO-FL levels are shown in Fig. 4.5(a) as a function of Co overlayer thickness. At a coverage as low as  $0.5$  Å of Co, we observe a clear shift (towards higher binding energies) and broadening of the HOMO level. With increasing Co layer thickness, Co  $3d$  states arise at the FL level and start dominating the spectrum. The Fermi edge becomes clearly visible at only  $10$  Å Co indicating that we do not have strong diffusion of the Co atoms, probably due to their high reactivity. However, at least the first monolayer of loose heringbone pentacene structure is mixed with Co. One may think now that the contact area between Co and pentacene is increased and the sensitivity of detecting the interfacial (band gap) states is increased. Even though it is difficult to assign the visible states between HOMO level and FL to pentacene band gap states or to Co, we believe that some of them can be attributed to hybridization between Co and pentacene energy levels.

Small penetration depth and symmetric energy level alignment were reported for the case of the Ca/pentacene/Ca interface [3], whereas Au and Ag showed significant diffusion and asymmetry. In [11] the authors investigated the diffusion of Ga atoms into 8-hydroxy-quinoline aluminium (Alq<sub>3</sub>) by tracking the Ga  $3d$

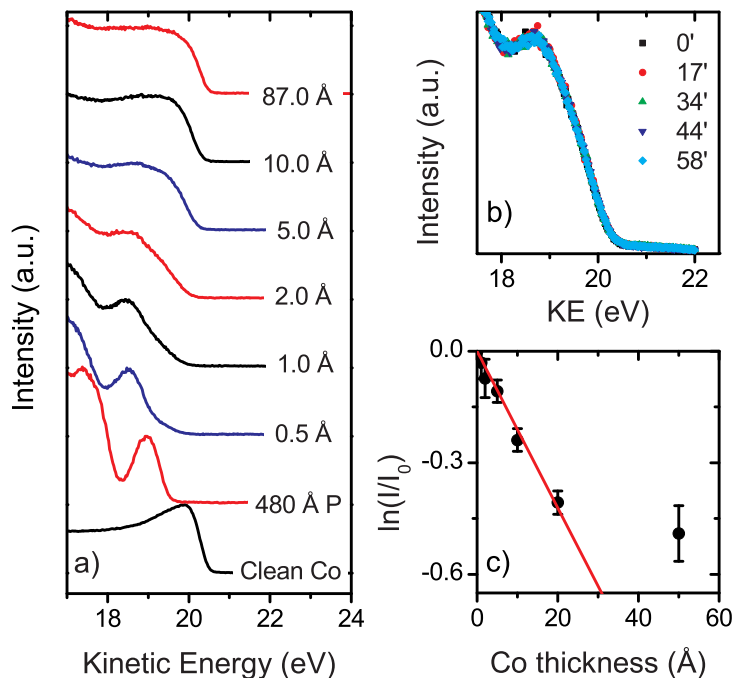


Figure 4.5: (a) UPS spectra of Co deposited on pentacene in the HOMO-FL region. Starting from the bottom: spectrum of clean Co, spectrum of 480 Å pentacene on Co and spectra with increasing Co thickness deposited atop. The labels indicate the Co thickness; (b) the time evolution of the spectrum in the HOMO level region at 2 Å Co coverage; (c) the attenuation of the intensity of the C 1s level of pentacene as a function of the top Co layer thickness investigated in 3 similar samples.

energy levels in time at 20 Å Ga coverage. They concluded that the diffusion of Ga takes place in time whereas for the more reactive Ca this is not the case. Similarly, we monitored the spectra around the Fermi level region as a function of time at only 2 Å Co coverage. The results are shown in Fig. 4.5(b). The spectra taken at a few intervals during one hour do not show any changes. UPS is very surface sensitive and diffusion of the Co atoms into pentacene taking place in time would leave a clear signature in the spectra, e.g. losing some intensity around 19.5 eV. This indicates that, apart from some initial intermixing, the Co atoms do not diffuse significantly in the pentacene layer. The attenuation of the C 1s level intensity with Co coverage is shown in Fig. 4.5(c) in a  $\ln(I_d/I_{d=0})$  vs.  $d$  plot, where  $d$  is the thickness of Co. Up to 20 Å of Co the intensity of C 1s signal

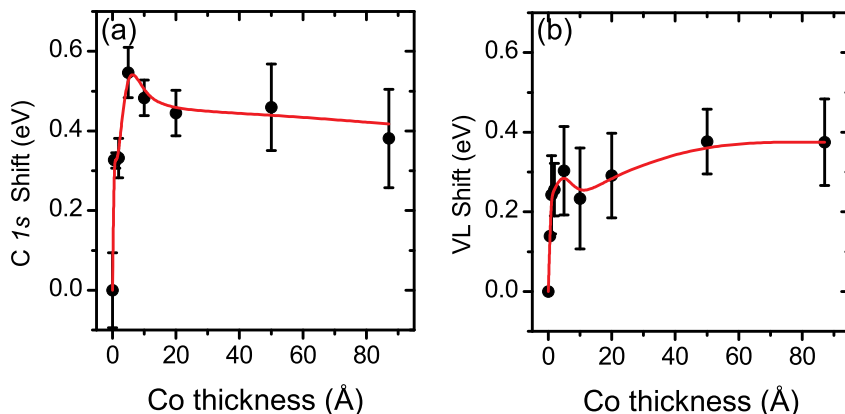


Figure 4.6: (a) C 1s energy level shift as a function of Co overlayer thickness, extracted from XPS. b) VL (SEC) shift, extracted from UPS. Added to figure is a guide to the eye which qualitatively represents the similar evolution of the energy levels in all the samples. Energy levels shift are expressed as  $BE(d) - BE(d = 0)$ , where  $d$  is the thickness of the Co layer.

is attenuated exponentially, given by the straight line in the  $\ln(I_d/I_{d=0})$  plot, consistent with a layer by layer growth of Co. Taking into account the angle of the detector with respect to sample surface normal we extract a value of  $\simeq 58$  Å for the mean free path of the photoelectrons, slightly higher than the mean free path of  $\simeq 43$  Å deduced from the attenuation of Si 2s level of the substrate in a test sample. The two values are expected to be similar since the kinetic energies of the photoelectrons are similar ( $\simeq 1200$  eV for C 1s and  $\simeq 1330$  eV for Si 2s). These observations plus the fact that the FL is visible at only 10 Å lead to the conclusion that diffusion length of Co in the pentacene layer is small. Starting with a coverage of about 20 Å the attenuation signal deviates from the exponential behavior. We believe that this represents the clustering of the Co atoms at the very rough (due to island growth of pentacene) surface layer.

We now turn our attention to the energy levels shift. At the first deposition step of 0.5 Å of Co, the HOMO, C 1s and VL shift towards higher binding energies, the VL shifts in the direction of work function decrease. In fact, the C 1s shift follows the shift of the HOMO level when the HOMO is still visible, therefore we use the position of C 1s to track HOMO for higher Co coverage when HOMO is not visible. As already mentioned we investigated this interface in several similar samples. In Fig. 4.6(a) and (b) we show the statistics for the C 1s and VL

shifts respectively. We mention that the Co energy levels (Co  $2p_{1/2}$ , Co  $2p_{3/2}$ ), as measured by XPS, do not show any significant change in binding energies for either of the two interfaces (not shown). Taking into account the C  $1s$  shift of about 0.4 eV at 87 Å Co, see Fig. 4.6, and the position of HOMO in Fig. 4.3 at 480 Å pentacene we find that the binding energy of C  $1s$  for P/Co interface is similar to that of Co/P interface. Therefore, we estimate a hole injection barrier of the same magnitude, namely 1.0 eV. Since up to 10 Å Co we do not have a metallic behavior yet, we understand the shift of the C  $1s$  as due to hybridization and/or as the classical shift of the FL through the band gap of pentacene due to the high density of surface states (Co and Co-P mixed states) which appear to be sufficient to pin the Fermi level. As seen in Fig. 4.6 the C  $1s$  shows a kinked behavior, similar to other metal (Au,Ca) on pentacene interfaces [3]. After 10 Å Co, which corresponds to the onset of the metallic behavior, the BE of C  $1s$  level decreases. We attribute this behavior to the metallic layer screening, i.e. a polarization energy contribution. Therefore, we conclude that at the other interface, Co/P, the C  $1s$  energy level position contains a polarization energy contribution as well. It could not be clearly assigned due to the Co-pentacene hybridization and due to the fact that at the surface layer the polarization energy is smaller since the vacuum is not polarizable, an effect which partially reduces the polarization energy.

The vacuum level shift follows qualitatively the C  $1s$  shift. With the onset of metallic behavior (+10 Å Co) the VL shift gradually increases. We ascribe this to a developing metal surface. After 20 Å Co there are relatively small variations in the VL position. However, the values of the work functions measured for the 3 samples differ from each other and are less than that of the bottom Co layer. The work function of the final surface is estimated to be about  $4 \pm 0.2$  eV taking into account the size of the error bars in Fig. 4.6b). As already pointed out the work function contains a contribution from the metal surface dipole. Given the island growth of the pentacene on Co and the clustering of Co when deposited on pentacene, it is expected that the final surface of the metallic layer has a high roughness. This leads to a lower work function of the top Co with respect to bottom Co, which is in agreement with our experiments. Similar behavior was reported for Au and Ag [3] when deposited on pentacene but it was not taken into account that the surface roughness may be responsible for such an effect.

The magnitude of the interfacial dipole at this interface is simply the difference between VL and C  $1s$  binding energy shifts [3]. This can be understood as follows. The C  $1s$  position depends only on the position of the FL in the band gap and it is not affected by any interfacial dipole (such as P/Co dipole or Co/vacuum dipole). With the deposition of Co the C  $1s$  level shifts and as a consequence (under the assumption of constant ionization potential of pentacene) the VL of

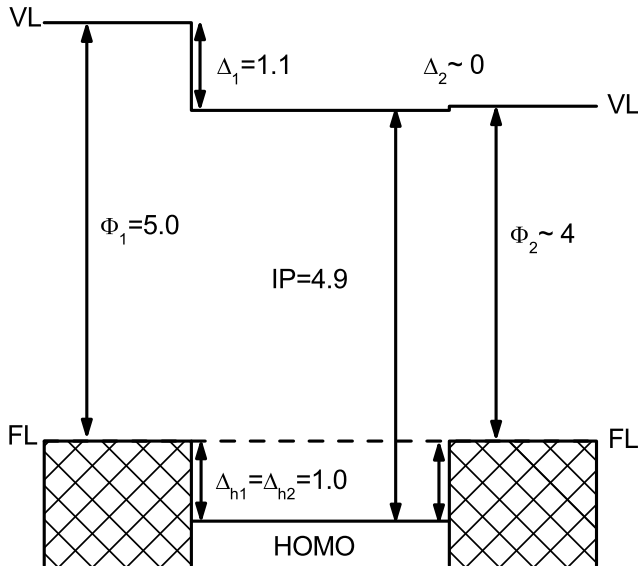


Figure 4.7: Band diagram for a layered Co/pentacene/Co structure. Lowest unoccupied molecular orbital (LUMO) of pentacene is not included.

the buried pentacene layer must follow the same shift. Therefore, in calculating the interfacial dipole one has to take the difference between the VL and the core level shift. Using Fig. 4.6 we estimate a value of  $\sim 0$  eV for the interfacial dipole at the P/Co interface, that is the vacuum levels align at this interface. This value is much smaller compared with 1.1 eV found for Co/P interface and can be explained by the diffusion of Co atoms and the high roughness of the interface. The interfacial dipole is now a sum of individual dipoles with random orientation.

## 4.4 Conclusions

Following the discussions in *Section 4.2* and *4.3* we are now able to construct a band diagram for a layered Co/P/Co structure, see Fig. 4.7. The band diagram is drawn in the frame of a model with interfacial dipoles [1–3,19]. The bending of pentacene bands is not included in figure since it is a small quantity and it was not clearly proven. Since the work function of the bottom and top Co layers were found to be different one may think that the Co/P/Co system can be described as a semiconductor sandwiched between two different metals. Given the IP of 4.9 eV for pentacene, a hole injection barrier of 1.0 eV and 4.0 eV for the Co work

function we get a value of 0.1 eV for the interfacial dipole at the P/Co interface in agreement with the discussion presented in the previous paragraph.

In this chapter we presented photoelectron spectroscopy investigations of the energy level alignment at Co/P/Co interfaces. At both interfaces signs of chemical interaction (hybridization) were found. At the sharp Co/P interface we found an interfacial dipole of 1.1 eV whereas the hole injection barrier amounts to 1.0 eV. In the case of the rough P/Co interface we estimated a  $\sim 0$  eV and 1.0 eV for the interfacial dipole and hole injection barrier, respectively. The hole injection barriers appear to be symmetric, an effect which we attributed to the very small diffusion of Co atoms in the pentacene layer, due to the high reactivity of Co. This in turn supports the idea of (strong) chemical interaction between Co and pentacene molecules. Polarization energy effects govern the energy level alignment in the bulk and at the interfaces. The interfacial dipole at P/Co interface was found to be smaller than that of the Co/P interface whereas the work function of the top Co layer was found to be  $\sim 1$  eV smaller than that of the smooth bottom Co layer, effects that we attribute to the high roughness and clustering of the Co atoms when deposited on pentacene.

For spintronics applications the existence of injection barriers may allow efficient injection of spin polarized carriers in pentacene under a bias when the barrier becomes triangular and carrier tunneling from Co to pentacene is possible. The extraction of the carriers at the P/Co interface is however not spin dependent. In this respect, building a spin valve with clean contacts remains problematic since both interfaces have to be spin dependent.

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