Chapter 3

A brief introduction to the system

In this work we focused our efforts on depositions of one molecule on two substrates. Among a variety of available molecules for organic-semiconductor devices, we have chosen to investigate one of the most studied [9]: 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA). Probably the main reason for which so many investigations have been done on PTCDA growth on various substrates, is that organic molecular beam epitaxy (OMBE) is feasible. PTCDA has a small vapor pressure at room temperature and it is thermally stable up to relatively high temperatures above 450 K. In this work most of the depositions of PTCDA have been made on the Ag(1 1 1) surface and some examples of the growth on the Au(1 1 1) surface will be added. In the first part of this chapter we present the basic knowledge regarding the molecule. Then we discuss some of the basic properties of OMBE of PTCDA on various substrates and conclude with a description of the interface properties of PTCDA on the Ag(1 1 1) and Au(1 1 1) surfaces.

All the information presented in this chapter has been taken or adapted from the literature.

3.1 The PTCDA molecule

A schematic picture of PTCDA is shown figure 3.1, and its empirical formula is $C_{24}O_8H_6$. The molecular structure can be simplified into two main regions: An aromatic core (perylene) of two anhydride groups (O═C—O—C═O). A summary of the

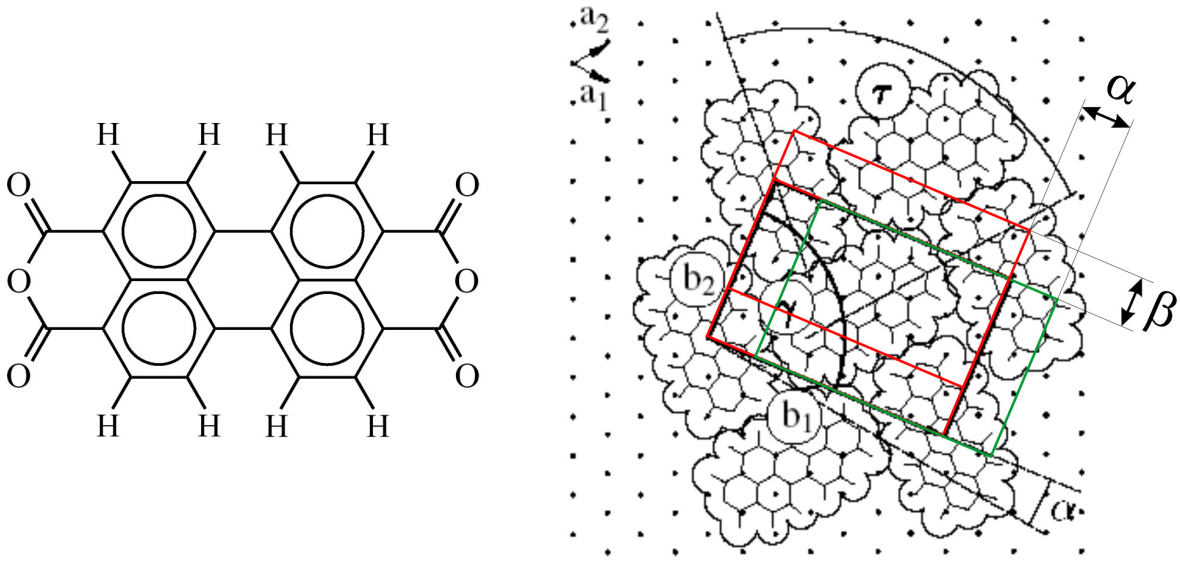

Figure 3.1: Left: Molecular structure formula of PTCDA. Right: real space adsorption model on Ag(1 1 1) [34, 35]

main properties of the PTCDA molecule, the bulk and the PTCDA/Ag(1 1 1) interface structure are given in table 3.1. Two polymorph bulk structures have been observed: α- and β-PTCDA [36]. In both structures the PTCDA molecules are lying flat in the (1 0 2) planes separated by the distance d(1 0 2). The molecular arrangement within these planes is known as the *herring bone* pattern. The different vertical stacking between the two polymorphic structures of PTCDA is shown on the right side of figure 3.1: α-PTCDA is shifted along b_1, while β-PTCDA is shifted along b_2 (see figure 3.1).

3.2 The Ag(1 1 1) and Au(1 1 1) surfaces: the work function

The properties of these two metal substrates have been deeply investigated and can be found in common solid state physics text books [1, 37]. We shall only address in this section the information that will be necessary for the understanding of the following chapters. First we discuss the work function.

Hüfner [1] reports a list of work functions ϕ for different metal surfaces measured

Table 3.1: Molecular and crystallographic properties of PTCDA. T_{KC} is the Knudsen cell temperature for the molecular beam deposition. Crystalline data adapted from [36]. Monolayer data adapted from [35].

Free molecule		
Mass (amu)	392	
Point group	D_{2h}	
T_{KC} (K)	623	
Bulk	α-PTCDA	β-PTCDA
Point group	C_{2h}	C_{2h}
a (Å)	3.74	3.78
b (Å)	11.96	19.30
c (Å)	17.34	10.77
d(1 0 2) (Å)	3.22	3.25
b_1 in the (1 0 2)-plane (Å)	19.91	19.30
b_2 in the (1 0 2)-plane (Å)	11.96	12.45
Volume ($Å^3$)	766.5	780.8
Unit cell area ($Å^2$)	238.1	240.3
Monolayer on Ag(1 1 1)		
b_1 (Å)		18.96
b_2 (Å)		12.61

Table 3.2: Work function ϕ of the Ag(1 1 1) and Au(1 1 1) surfaces adapted from [1]. The values $\Delta\phi$ refer to the change in work function upon deposition of one layer of PTCDA on the (1 1 1) surfaces (adapted from [38]).

Silver	ϕ (eV)	Gold	ϕ (eV)
(1 1 1)	4.74	(1 1 1)	5.31
(1 1 0)	4.52	(1 1 0)	5.37
(1 0 0)	4.64	(1 0 0)	5.47
polycrystal	4.26	polycrystal	5.1
$\Delta\phi$	+0.1	$\Delta\phi$	-0.5

with high resolution photoelectron spectroscopy. The values for silver and gold are found in table 3.2. There are a number of general comments regarding the work function that are useful for our discussions in the following chapters. Notice from the table that the work functions change significantly for different surfaces. The differences between the extreme cases of the (1 1 1) and polycrystalline surfaces is as high as 0.5 eV for silver and 0.2 eV for gold. The consequence of such differences is a strong indication that the details of the preparation of a surface, i.e. the step density and in general the presence of defects and impurities, may significantly influence the results. The work functions for the clean surfaces and covered by one layer of PTCDA have been measured by [38]. We will adopt only the relative changes, between clean surface and covered by one layer. The work functions of the two (1 1 1) surfaces covered by one layer of PTCDA are, within experimental error, the same: 4.8 eV.

Of the two metals, only the Au(1 1 1) is reconstructed. It shows a $(22 \times \sqrt{3})$ discussed in detail by *Barth et al.* [39] and shown in a Scanning Tunneling Microscopy (STM) image in figure 3.2. With such a large reconstructed unit cell we expect to find diffraction spots very close to the (0 0) reflected beam. The distance between the *elbows* of the reconstructed surface is 28 nm.

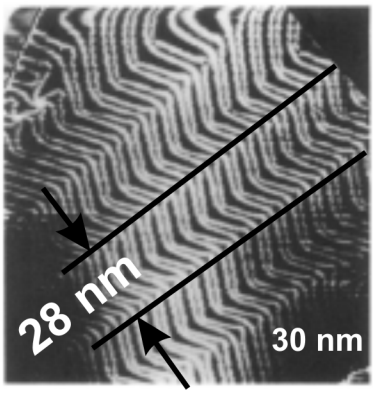

Figure 3.2: Scanning Tunneling Microscopy image of the Au(1 1 1)—$(22 \times \sqrt{3})$ surface reconstruction. The distance marked between the *elbows* of the reconstructed surface is of 28 nm. Adapted from [39].

3.3 PTCDA on Ag(1 1 1)

The first epitaxial PTCDA growth studies have been reported for ionic crystal substrates [40] and graphite (0 0 0 1) [41]. Due to a strong substrate-adsorbate interaction (enhanced by the functional groups), the growth on semiconductors, such as Si(1 1 1) and GaAs(1 0 0), results in disordered structures [42, 43, 44]. It has been shown for GaAs(1 0 0) that upon passivation with Se the reactivity of the surface decreases and ordered layers are grown [43, 45].

However, the most investigated substrates are the noble metal surfaces ([43] and references therein). The deposition of PTCDA on Au(1 1 1) and Ag(1 1 1) leads to long-range ordered structures [46]. However, the Ag(1 1 1) surface provides an inert and smooth support which favors the growth of ordered crystallites with the molecules lying *flat*, i.e. with the (1 0 2) surface parallel to the substrate, for thicknesses up to 100 nm.

Glöcker et al. [35] have shown that the commensurate PTCDA monolayer unit cell on the Ag(1 1 1) differs from the (1 0 2) unit mesh by only a very little amount. The origin of the commensurability of the PTCDA monolayer is caused by a site specific bond of the molecules to the substrate which has been characterized by high-resolution Low Energy Electron Diffraction (SPA-LEED), XPS, UPS, NEXAFS, EELS, HREELS, STM and AFM (see appendix for a list of acronyms) [34, 47, 48, 49, 50].

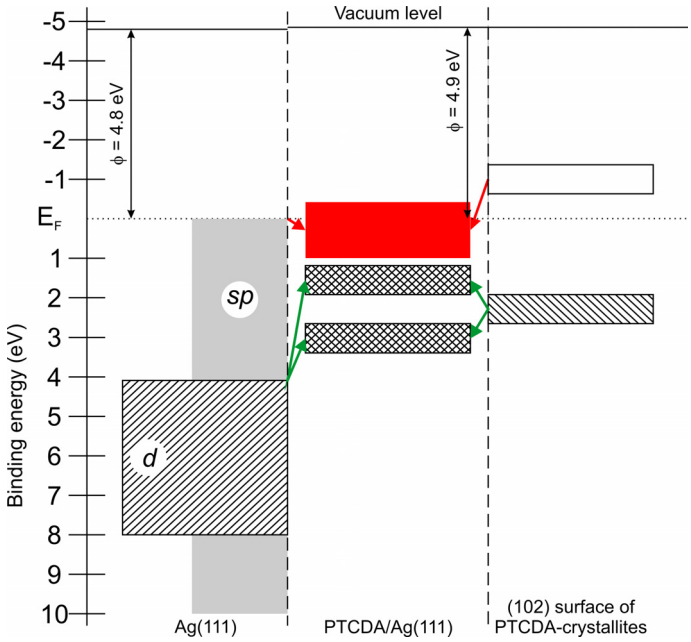

Figure 3.3: Schematic view of the electronic states of the clean Ag(1 1 1) surface, the first PTCDA layer on the Ag(1 1 1) surface and the (1 0 2) surface of crystalline PTCDA on Ag(1 1 1). The top line indicates the vacuum level for each system. Assuming no charging and field effect, the Fermi level is constant (dotted lines).

A summary of the bond properties [47] is found in figure 3.3.

A temperature dependent growth mode transition from a Frank-van der Merwe (layer-by-layer) to Stranski-Krastanov (SK) has already been reported for PTCDA on the Ag(1 1 1) [51, 52, 53, 54]. The smooth transition occurs at ~ 340 K.