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# Pentacene/Cu(110) interface formation monitored by *in situ* optical spectroscopy

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The adsorption of pentacene on the Cu(110) surface has been investigated by reflectance difference spectroscopy (RDS) and spot profile analysis low energy electron diffraction (SPA-LEED). The sensitivity of RDS to electronic transitions involving both surface states and intramolecular transitions allows a close monitoring of the formation of interfacial electronic states and structural phase transitions of the pentacene monolayer on Cu(110).

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## I. INTRODUCTION

The interface between an organic thin film and a metal surface plays a crucial role in the performance of optoelectronic devices based on organic semiconductors such as field-effect transistors, photovoltaic cells, and light-emitting diodes [1–5]. Due to the large number of internal degrees of freedom of the aromatic organic molecules and the delicate interplay between the molecule-molecule and molecule-substrate interactions, the geometric structures and electronic structures of the first molecular layer are rather complex. In order to reveal the structural and electronic details of the organic/metal interfaces, extensive studies have been performed using a variety of surface analytical techniques such as scanning tunneling microscopy/spectroscopy (STM/STS), ultraviolet photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPS), near edge x-ray absorption fine structure (NEXAFS), low energy electron diffraction (LEED), photoemission electron microscopy (PEEM), and low energy electron spectroscopy (LEEM). This has led to a significantly improved understanding of the complex structural phase diagrams of organic adlayers [6–11]. Moreover, recent studies on the electronic interaction between organic adsorbates and metal substrates have provided new insight concerning the interfacial states present in strongly interacting system [12–16]. Besides the surface analysis methods mentioned above, optical spectroscopy in the visible range has been proved to be very valuable in linking the structural with the electronic and optical properties of the interface [17,18]. Reflectance difference spectroscopy (RDS), also called reflectance anisotropy spectroscopy (RAS), measures the difference in the normal-incidence reflectance for two perpendicular orientations of the polarization vector as a function of photon energy [19]. For substrates with cubic symmetry, for which the bulk is optically isotropic, a nonvanishing RD signal arises from the near surface region of an anisotropic surface only. In this case, RDS is extremely sensitive to the electronic structure of the surface, in contrast to the conventional linear optical spectroscopic techniques [20,21]. Likewise, RDS is also quite sensitive to the optical anisotropy arising from intramolecular electronic transitions of adsorbed organic molecules allowing the determination of their in plane orientation [22–24]. By combining these two capabilities, we explore the potential of RDS as a sensitive *in situ* probe to monitor, *in real time*, the formation of the organic/metal interface.

As one of the model systems, the adsorption of pentacene molecules on the Cu(110) surface has been studied extensively both experimentally and theoretically. Several different structural phases have been reported for the pentacene monolayer adsorbed on Cu(110) depending on the preparation conditions. Söhnchen *et al.* and Lukas *et al.* have reported the coexistence of $p(6.5 \times 2)$ and $c(13 \times 2)$ structures at elevated temperatures for pentacene monolayers prepared by controlled multilayer desorption [25,26]. More recently, Müller *et al* and J. Kartínez-Blanco *et al.* have shown that at room temperature the pentacene adlayer structure changes from a two-dimensional lattice gas phase at low coverages into a relatively well ordered $(7 \times 2)$ phase at 0.8 ML and finally to a $\binom{6\ 1}{1\ 4}$ phase at 1 ML, where 1 ML (monolayer) is assigned to the completion of the high coverage $\binom{6\ 1}{1\ 4}$ [27,28]. The electronic coupling between pentacene and the Cu(110) substrate and its effects on the interfacial electronic structures have also been investigated. Scheybal *et al.* have shown that pentacene adsorption induces a downward shift in the energy of the Shockley type occupied surface state [29]. Valence-level photoemission studies by Yamane *et al.* showed evidence for the formation of the interface states with pronounced two-dimensional energy-band dispersion [14]. Furthermore, the NEXAFS investigation performed by Lukas *et al.* revealed a broadened $\pi^*$-resonance line shape for monolayer pentacene on Cu(110) which is in a strong contrast to the well separated multiple peaks observed for pentacene in the gas phase and in the bulk crystalline phases [25,26,30].

## II. EXPERIMENT

The experiments were carried out in a UHV chamber with a base pressure of $1 \times 10^{-10}$ mbar. The Cu(110) substrate can be heated to 1000 K by electron beam bombardment and cooled down using a liquid nitrogen cryostat. The clean Cu(110) surface was prepared by sputtering with 900 eV $Ar^+$ ions and subsequent annealing to 800 K. The cleanliness and the surface crystalline quality was checked by reflectance difference spectroscopy (RDS), Auger electron spectroscopy (AES), and spot profile analysis low energy electron diffraction (SPA-LEED), respectively. The pentacene molecules were evaporated from a thoroughly degassed organic molecular

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beam epitaxy source equipped with three Knudsen cells. The growth is monitored *in situ* using a photoelastic modulator (PEM) based RD spectrometer [31,32]. The normalized difference in reflectance defined as

$$\frac{\Delta r}{r} = 2\,\frac{r_{[1\bar{1}0]} - r_{[001]}}{r_{[1\bar{1}0]} + r_{[001]}} \tag{1}$$

is recorded either in spectroscopic mode over a photon energy range between 1.5 and 5.5 eV or by recording transients where the $\Delta r/r$ signal at a selected photon energy is measured as a function of time. In addition, the crystalline structure of the deposited pentacene layer was investigated at 150 K using SPA-LEED. One monolayer (ML) coverage in this paper corresponds to a pentacene layer with a $\begin{pmatrix} 6 & 1 \\ 1 & 4 \end{pmatrix}$ superstructure, i.e., a density of $8.7 \times 10^{13}$ molecules/cm$^2$. This is the most densely packed monolayer structure that can be formed when adsorbing pentacene on Cu(110) at room temperature [27].

## III. RESULTS AND DISCUSSION

### A. Spectroscopic evolution of the electronic structure at the interface

#### 1. *Pentacene induced modification of the surface states and surface modified bulk states of Cu(110)*

Figure 1 shows the real part of the RD spectrum recorded from the clean Cu(110) surface and its evolution upon successive deposition of pentacene at room temperature, up to a thickness of 1.12 ML. The pronounced optical anisotropy peaked at 2.1 eV on the bare Cu(110) surface derives from three different contributions, namely, electronic transitions from occupied to unoccupied surface states localized at the $\bar{Y}$ point of the surface Brillouin zone, surface modified bulk interband transitions, and intraband transitions, respectively [19–21,33,34]. Among these contributions, the surface state related transition is the dominant one and is extremely sensitive to surface defects and adsorbates [34,35]. The surface states related contribution makes the RD signal at 2.1 eV a very sensitive probe of adsorbates or surface defects. Indeed, upon adsorption of the pentacene molecules on the Cu(110) surface, the RD intensity at 2.1 eV decreases continuously until a steady state is reached after a deposition time just below 30 min (thin green dashed line). This indicates that the surface is fully covered with a closed layer of pentacene after a deposition time of about 27 to 30 min. As we will show later, this point corresponds to the completion of a pentacene monolayer with a (7 × 2) crystalline structure, i.e., a density of $7.8 \times 10^{13}$ molecules/cm$^2$. The modification of the *occupied* surface state involved in the surface state transition at 2.1 eV has previously been investigated using high-resolution angle-resolved UPS by Scheybal *et al.* They have shown that the population of the Cu(110) surface state is not quenched, but rather increased due to a downward shift in energy upon pentacene adsorption [29]. Consequently, the quenching of the RD signal at 2.1 eV observed in Fig. 1 must be due to the strong perturbation of the *unoccupied* surface state involved in this transition [20]. A closer inspection of the evolution of the 2.1 eV RD signal reveals a small blue shift of the peak position in addition to the decrease of its amplitude. The sign and the amplitude of the shift observed here coincidences nicely with the downward shift of the Shockley state of around 80 meV as reported in [29]. Note, however, that the modification of the optical anisotropy derives not only from the surface states but also from surface modified bulk states that could also be affected by pentacene adsorption. Anyway, the energy shift suggests an electronic hybridization between Cu(110) and pentacene electronic states.

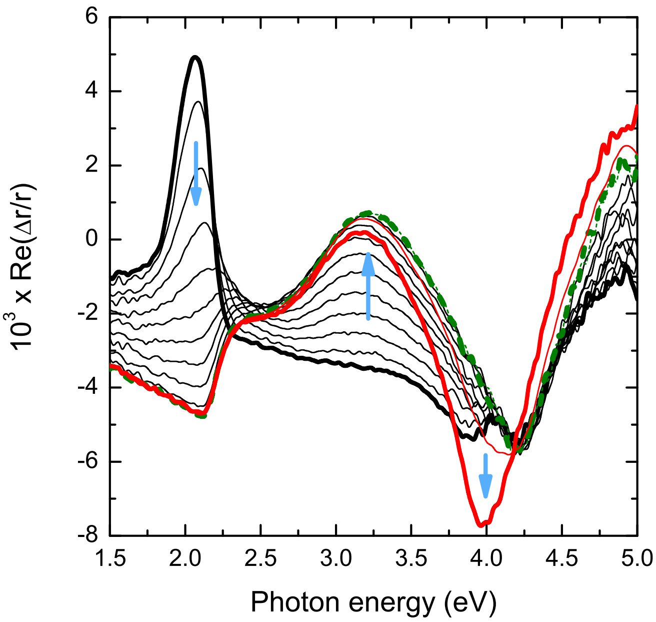

FIG. 1. (Color online) Real part of the RD spectrum recorded from the clean Cu(110) surface (thick black solid line) and its evolution upon successive deposition of pentacene at room temperature. The pentacene coverage was increased in steps of about 0.086 ML (3 min deposition time) up to a final thickness of around 1.12 ML (39 min deposition time in total). The spectra recorded at 30, 33, 36, and 39 min are plotted using a thin green dashed line, a thick green dashed line, a thin red solid line, and a thick red solid line, respectively. The decay of the 2.1 eV peak as well as the growth of the 3.2 and the 3.9 eV peaks are indicated by the arrows.

#### 2. *Formation of the pentacene $\pi^*$-derived electronic resonance*

Besides the strong modification of the electronic structure of the Cu(110) surface, the molecular electronic properties of the pentacene molecules is also strongly affected at the interface. Actually, no RD signal originating from direct intramolecular transitions is observed for the pentacene molecules adsorbed in the first monolayer. Instead, only a broad feature around 3.2 eV can be discerned in the RD spectra in Fig. 1. The amplitude of this feature increases linearly with pentacene coverage until the surface is covered by a pentacene monolayer with a (7 × 2) structure. This RD feature, however, cannot be attributed to the pristine pentacene intramolecular transition, neither by its energetic position nor by its polarization state. Besides, the peak is much broader in comparison with the RD signature expected for an intramolecular transition, as we will see later. We tentatively attribute this RD feature to electronic transitions to the pentacene $\pi^*$-derived valence resonance. In fact, it is known from the Anderson-Newns model of chemisorption [36,37] that weak and moderately strong hybridization of adsorbate localized valence orbitals with broad substrate bands leads to a formation of resonances whose width depends on the strength of the adsorbate-substrate coupling [38–44]. Besides, such adsorbate-derived resonances may be partially occupied via charge transfer from the substrate into the resonance states lying below the Fermi level of the system [36,43]. For example, the $2\pi^*$ resonance model has been used successfully to interpreted the electronic interaction between carbon monoxide (CO) and metal substrates including Cu(110) [43]. Indeed, in a previous RDS study of CO adsorption on Cu(110) we have observed a very similar optical feature as in Fig. 1 which we interpreted in terms of electronic transitions from the occupied stats at Fermi level into the CO $2\pi^*$-derived resonance state on Cu(110) [45]. In that case, the hybridization of CO $2\pi^*$ orbital with the substrate $s$, $p$, and $d$ bands induces a resonance state peaked at about 3.3 eV above the Fermi energy [43]. Similar $\pi^*$-resonance states have also been observed upon adsorption of aromatic hydrocarbon molecules such as benzene [46,47] and PTCDA (3,4,9,10-perylene-tetracarboxylic) [12,13] on metal surfaces. Considering the adsorption of pentacene molecules on copper surfaces, electronic coupling between molecules and substrates has been reported based on both experimental and *ab initio* investigations [14–16]. In particular, for the adsorption of pentacene molecules on the Cu(110) surface, there is experimental evidences for the formation of the $\pi^*$-resonance states. Actually, it has been clearly demonstrated by NEXAFS that the $\pi^*$-resonance line shape, which is due to the transitions from the C $1s$ level into unoccupied states of pentacene molecules in the first monolayer on Cu(110) differs clearly with that measured from multilayer pentacene [25,26]. In this case, the multiple NEXAFS peaks observed in the thick pentacene films collapse into a single broad peak [25,26]. Simultaneously, investigations of the occupied electronic states using UPS reveal an increased electronic population at the Fermi energy $E_F$ upon pentacene monolayer adsorption [14]. The observed steplike feature near $E_F$ has been suggested by Yamane *et al.* as the LUMO (lowest unoccupied molecular orbital) derived state which is partially occupied by negative charge transfer from the substrate. These experimental observations can be explained by the formation of the pentacene $\pi^*$-derived resonance due to the the hybridization of the pentacene $\pi^*$ orbital with the spatially overlapping electronic bands of Cu(110).

Upon a closer look at the evolution of the RD spectra presented in Fig. 1, it can be recognized that the RD spectra recorded after 30 min (thin dashed green line) and 33 min (thick dashed green line) pentacene deposition are identical. From the LEED studies discussed later we can infer that these two spectra correspond to surface coverages corresponding to a pentacene monolayer dominated by a $(7 \times 2)$ and a $\begin{pmatrix} 6 & 1 \\ 1 & 4 \end{pmatrix}$ structure, respectively. The RD feature corresponding to the pentacene $\pi^*$-derived resonance peaked at 3.2 eV increases linearly with the pentacene coverage but only till completion of the $(7 \times 2)$ monolayer phase. This observation illustrates that the $\pi^*$-derived resonance is localized at the interface between the pentacene monolayer and the Cu(110) substrate. Once the surface is completely covered, further increasing the surface packing density of pentacene and changing the adlayer structure from the $(7 \times 2)$ into the $\begin{pmatrix} 6 & 1 \\ 1 & 4 \end{pmatrix}$ phase has no observable influence on the electronic hybridization between pentacene and Cu(110). The result is in line with the fact that the RD signal around 2.1 eV, which is sensitive to the modification of surface electronic structure of Cu(110) (including both surface states and surface modified bulk states), also remains unchanged for the spectra recorded after 30 and 33 min, respectively. Therefore, one can conclude that increasing the surface density of the pentacene does not necessarily enhance the electronic coupling between pentacene molecules and the Cu(110) substrate. We would also like to mention that similar RD features associated with the $\pi^*$-derived resonance due to the hybridization of aromatic molecules and metal substrates have also been observed in case of the adsorption of para-sexiphenyl [48] and perfluoropentacene on Cu(110) [49].

#### *3. The onset of the pentacene intramolecular transition*

Upon further deposition of pentacene, a negative RD peak at around 3.9 eV starts to develop in the RD spectra recorded after 36 min of deposition. From the energetic position this RD peak can be attributed to the intramolecular transition from the HOMO (highest occupied molecular orbital) to the LUMO + 2 (the third lowest unoccupied molecular orbital) of pentacene [50,51]. As we have discussed in the last paragraph, the molecular orbitals of pentacene molecules in the first monolayer couple with the electronic states of Cu(110) and form hybrid electronic states. Consequently, the pristine intramolecular transition of pentacene can only be found for molecules which are decoupled from the substrate. Obviously this condition is fulfilled already for the pentacene molecules in the second monolayer [17]. Noting that the dipole moment of the corresponding transition is along the long molecular axis, the negative sign of the RD signal at 3.9 eV implies that the pentacene molecule in the second monolayer are preferentially aligned along the $[1\bar{1}0]$ direction of the substrate. This result fully agrees with the conclusion drawn from the previous LEED and NEXAFS studies on the same system [25,26].

### B. Structural phase transition at the interface

In order to study the adsorption phase diagram in more detail, the real part of the RD signal at photon energies of 2.1 and 3.9 eV were recorded *in situ* during pentacene deposition on Cu(110). Both RD transients are plotted in Fig. 2 as a function of deposition time. In this experiment, a slightly higher deposition rate was used. The real part of the RD signal at 2.1 eV decreases gradually and is finally quenched after 25 min of deposition indicating that the Cu(110) is fully covered by pentacene molecules. On the other hand, the RD signal at 3.9 eV only starts to grow after 30 min of pentacene deposition. As we have already discussed, the full quench of the RD signal at 2.1 eV should correspond to the moment that the surface is completely covered by pentacene. In contrast, the appearance of the RD peak at 3.9 eV, which is the sign of the onset of the second monolayer growth, is delayed by 5 min. The observed delay between the complete covering of the Cu(110) surface by pentacene and the onset of the growth of the second monolayer shows the existence of two structural phases for the full pentacene monolayer, an unconstrained phase with lower molecule density which is completed after 25 min and a dense (constrain) phase which is

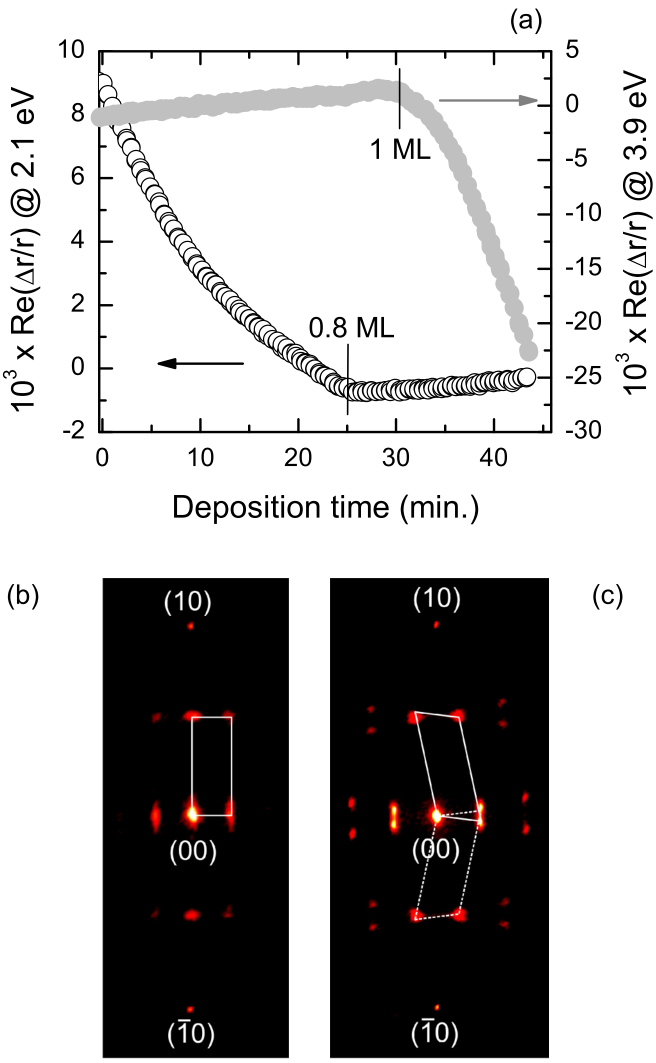

FIG. 2. (Color online) (a) Real part of the RD signals at 2.1 and 3.9 eV recorded during pentacene adsorption at room temperature on the Cu(110) surface. The corresponding SPA-LEED images recorded at pentacene coverages of 0.8 and 1 ML are displayed in (b) and (c), respectively. The frame of the white lines in (b) and (c) mark the unit cells of the $(7 \times 2)$ and the $\left(\begin{smallmatrix}6 & 1\\ 1 & 4\end{smallmatrix}\right)$ structures, respectively. The dashed line in (c) indicates the mirror domain. An electron beam energy of 90 eV has been used for the SPA-LEED measurement.

completed after 30 min of pentacene deposition. According to the measured offset of ∼5 min, the density of the unconstrained phase should be $\sim 25/30 \approx 0.83$ of that of the constrained phase. Based on the ratio of the pentacene molecule density, these two phases can be assigned to the $(7 \times 2)$ and $\left(\begin{smallmatrix}6 & 1\\ 1 & 4\end{smallmatrix}\right)$ phases reported by Müller *et al.* [27]. Indeed, the results of SPA-LEED measurements performed on the Cu(110) surface after a pentacene deposition of 25 min [Fig. 2(b)] and 30 min [Fig. 2(c)] show the diffraction patterns characteristic of the $(7 \times 2)$ and the $\left(\begin{smallmatrix}6 & 1\\ 1 & 4\end{smallmatrix}\right)$ phase, respectively. The sharp diffraction spots indicate the formation of long range ordered pentacene layers with the corresponding superstructure.

## IV. CONCLUSION

In conclusion, we have shown that the formation of the pentacene/Cu(110) interface can be monitored in *real time* using *in situ* reflectance difference spectroscopy. RDS is sensitive to the electronic transitions involving pristine electronic states of metal substrates, interface states formed upon organic molecule adsorption, and the intramolecular transitions of organic molecules. This makes RDS a powerful tool for *in situ* studies of the formation of the interface between organic molecules and metal substrates concerning both morphological and electronic aspects. From the RD signatures derived from the surface state transition of the substrate and the intramolecular transition of pentacene as probes of the bare Cu(110) surface fraction and the onset of the second monolayer growth, respectively, the completion of the $(7 \times 2)$ and $\left(\begin{smallmatrix}6 & 1\\ 1 & 4\end{smallmatrix}\right)$ phases within the first pentacene monolayer can be determined precisely. Regarding the electronic structures, RD spectra reveal the perturbation of the unoccupied surface state of Cu(110) and the formation of hybrid interfacial electronic states upon pentacene adsorption.

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