

# Molecular Orientation and Ordering during Initial Growth of Copper Phthalocyanine on Si(111)

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The molecular orientation and order in the initial growth of copper phthalocyanine on Si(111) was investigated *in-situ* by angular-dependent X-ray absorption spectroscopy. A transition from lying-down to standing-up configuration occurs in less than one monolayer. After the Si surface is passivated by a monolayer of the molecules, only the standing-up structure persists in subsequent growth. The molecular film also exhibits an order-disorder-order transition in the distribution of molecular tilt angle during growth. These transitions are related to the changes of interactions in the system at different stages.

**KEYWORDS:** organic film, X-ray absorption, tilt angle, interaction

## 1. Introduction

The nucleation and growth of organic molecular thin film systems has been shown to demonstrate qualitative differences to that for inorganic systems<sup>1-4</sup>. The orientational degree of freedom for molecules with respect to the lying-down ( $\lambda$ ) and standing-up ( $\sigma$ ) configurations during the growth of organic films is one of the most important differences<sup>2</sup>. The orientation may change from one layer to the next, or even within a given layer. Such disorder in the growth of molecular systems can affect their electronic transport properties<sup>5</sup>. Whilst the growth of inorganic systems is now understood with a certain level of sophistication, the understanding of new effects introduced by orientational and conformational degrees of freedom on the growth of molecular systems is in its infancy<sup>1-4, 6-8</sup>.

Angular-dependent X-ray absorption spectroscopy (XAS) is a powerful tool for determining molecular orientation in organic layers, even at sub-monolayer coverages<sup>9-11</sup>. The molecular tilt angle within a layer can be calculated using absorption intensities at various incident angles. Petrovykh et al.<sup>12</sup> recently studied DNA self-assembled monolayer by angular-dependent XAS and concluded that the molecular orientational order of a layer can be derived from detailed analysis of XAS measurements. Kafer et al.<sup>3</sup> reported that XAS is sensitive to the conformational degree of freedom that is found only in the growth of organic systems.

Copper phthalocyanine (CuPc) is a model system for an entire class of low molecular weight, flat, organic molecules<sup>13</sup>. Thick ordered phthalocyanine films have been grown on various substrates<sup>14-17</sup> and the adsorption behaviors of CuPc molecules on Si(111) and Si(100)<sup>18,19</sup> have been previously studied by scanning tunneling microscopy (STM). In this study, we report the *in situ* nucleation of CuPc on Si(111)-(7x7) by angular-dependent XAS, with particular attention to the evolution of molecular orientation and order in the first few layers. Only the  $\lambda$  phase nucleates at the early stage of growth due to the strong interaction between the CuPc and Si. The Si 2p and C 1s core level spectra reveal that the

molecules in the first monolayer are strongly coupled to the surface. The coexistence of the  $\sigma$  and  $\lambda$  structures is observed at half monolayer coverage, continuing until the Si surface is completely passivated. Pure  $\sigma$  nucleation dominates the late growth stage, and at the same time improved orientational order of the layers is observed.

## 2. Experimental Section

Clean Si(111)-(7x7) surfaces were obtained by degassing samples at  $\sim 600$  °C for 8-12 hours and then flash annealing at  $\sim 1200$  °C for 15 s with direct current sample heating in an ultra-high vacuum chamber with a base pressure of about  $2 \times 10^{-10}$  Torr. Copper phthalocyanine (CuPc) powder with a purity of 99.99 % was purchased from Sigma-Aldrich Inc. After being degassed at 200 °C for 24 hours in a standard Knudsen cell, CuPc was then sublimed *in-situ* onto clean Si(111)-(7x7) at room temperature. The source temperature was 380 °C and the chamber pressure was less than  $2 \times 10^{-9}$  Torr during deposition.

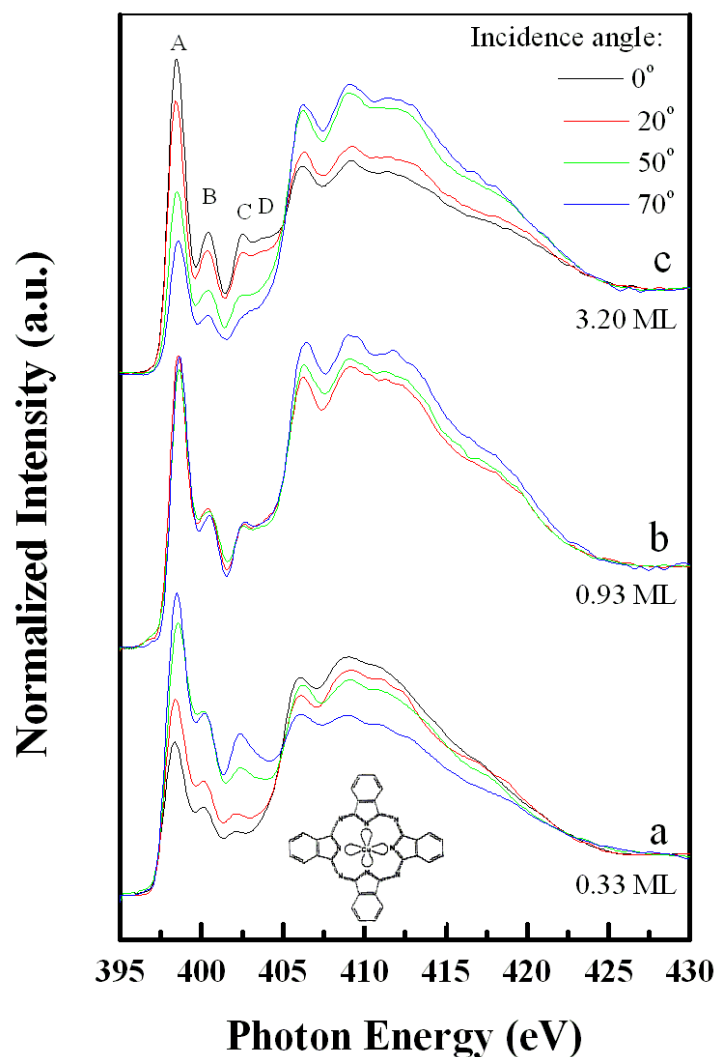
X-ray absorption (XAS) and photoemission (PES) measurements were performed at the SINS beamline, Singapore Synchrotron Light Source <sup>20</sup>. The total instrument resolution for PES, estimated from the Fermi edge broadening of a Au foil electrically attached to the sample holder is  $\sim 150$  meV. The x-ray absorption experiments were performed in partial yield mode with photon energy resolution of 0.1 eV. All the XAS spectra are normalized to constant absorption edge step height. The film thickness is estimated from the attenuation of the Si 2p signal taken at normal emission geometry with a photon energy of 650 eV. To prepare one monolayer CuPc on Si(111), a thick, bulk-like layer of CuPc was annealed at 300 °C; a procedure analogous to that used to form a C<sub>60</sub> monolayer on Si surface <sup>21</sup>.

### 3. Results and Discussion

Figure 1 shows the angular-dependence of N K-edge XAS spectra at various coverages. The incidence angle is defined as the angle between the direction of incident photons and the normal of the substrate. Each spectrum has absorption features consistent with previous reports<sup>14, 15</sup>, although the relative intensities for these features are angle-dependent. The first four sharp absorption peaks (A, B, C, D) are assigned to excitations from N 1s core level to individual  $\pi^*$  states, and the broad absorption features at the higher photon energy side correspond to transitions to  $\sigma^*$  states. In Fig.1a, the maximum intensity of the  $\pi^*$  resonances is observed at grazing incidence; whereas the intensities of the  $\sigma^*$  resonances reach the maximum at normal incidence. The molecular structure of CuPc clearly shows that the  $\pi^*$  and  $\sigma^*$  orbitals are directed essentially out-of-plane and in-plane respectively, indicating that the CuPc molecular plane is nearly parallel to the Si surface. Therefore, the molecules at 0.33ML coverage adopt the lying-down configuration ( $\lambda$  structure).

A transition from  $\lambda$  structure to  $\sigma$  structure is observed with increasing coverage. When the coverage increases to almost 1 ML, the angular-dependence of the  $\pi^*$  resonances almost vanishes while the intensities of the  $\sigma^*$  resonances are slightly angular-dependent, as shown in Fig.1b. This could mean that all molecules in this layer adopt a magic tilt angle ( $55^\circ$  from ref. 9), or the molecular orientation in this layer is disordered without a fixed tilt angle. In our study, the CuPc layer is deposited cumulatively on the Si substrate by increasing the deposition time in sequential steps. The XAS measurement is averaged over the whole layer and the signals in Fig.1b actually include the contributions from both the sample with 0.33 ML of the  $\lambda$  structure, as well as the additional add-on molecules. Our density functional theoretical calculations show that it costs about 2.5 eV to force a molecule from lying-down configuration to a configuration with the magic tilt angle. The intermolecular interaction cannot drive this configurational change. As a consequence, the molecules with initial lying-down configuration

remain essentially unperturbed during later growth. To achieve the disorder-like angular-dependent XAS spectra, the molecules deposited later must be in standing-up configuration ( $\sigma$  structure). The molecular orientation for the monolayer is therefore, on average, disordered. The fact that the orientation in this monolayer appears disordered indeed reflects the coexistence of  $\sigma$  and  $\lambda$  structures. From the viewpoint of structure, the monolayer appears strongly inhomogeneous due to the coexistence of both  $\sigma$  and  $\lambda$  structures in this layer, which could account for the small dichroism of the  $\sigma^*$  resonances in the spectra.



**Figure 1.** Angular-dependent N K-edge x-ray absorption spectra for CuPc layer on Si surface at various coverages. All spectra are normalized to have the same absorption edge step height. The incidence angle here is defined as the angle between the incident direction of photons and the normal direction of the Si surface. The inset shows the schematic structure of CuPc molecule.

The situation changes dramatically beyond one monolayer coverage. Figure 1c shows the angular-dependent XAS spectra at a coverage of 3.20 ML. It is obvious that the angular-dependence of the  $\pi^*$  and  $\sigma^*$  resonances are completely in reverse to those at 0.35 ML (Fig.1a). This clearly suggests that the detected layer becomes ordered again with all the molecules in standing-up configuration ( $\sigma$  structure).

The molecular orientational order of an organic layer can be also extracted from angular-dependent XAS spectra. Petrovykh et al.<sup>12</sup> proposed that molecules have a certain tilt associated with a Gaussian distribution rather than a fixed tilt angle which is normally assumed in most XAS analyses<sup>9</sup>. To take the distribution of molecular orientation in account, the widely accepted formula in ref. 9 has been revised as follows<sup>12</sup>:

$$I(\theta, \tau, \delta) = \int_0^{2\pi} d\phi \int_0^{\pi} d\omega \sin(\omega) P(\omega, \tau, \delta) \left\{ \cos\left(\theta + \frac{\pi}{2}\right)^2 \cos(\omega)^2 + \sin\left(\theta + \frac{\pi}{2}\right)^2 \sin(\omega)^2 \cos(\phi)^2 + \frac{1}{2} \sin(2\theta + \pi) \sin(2\omega) \cos(\phi) \right\}$$

where  $\theta$  is the incidence angle and  $\tau$  the tilt angle.  $P(\omega, \tau, \delta)$  is a Gaussian distribution normalized over the unit sphere

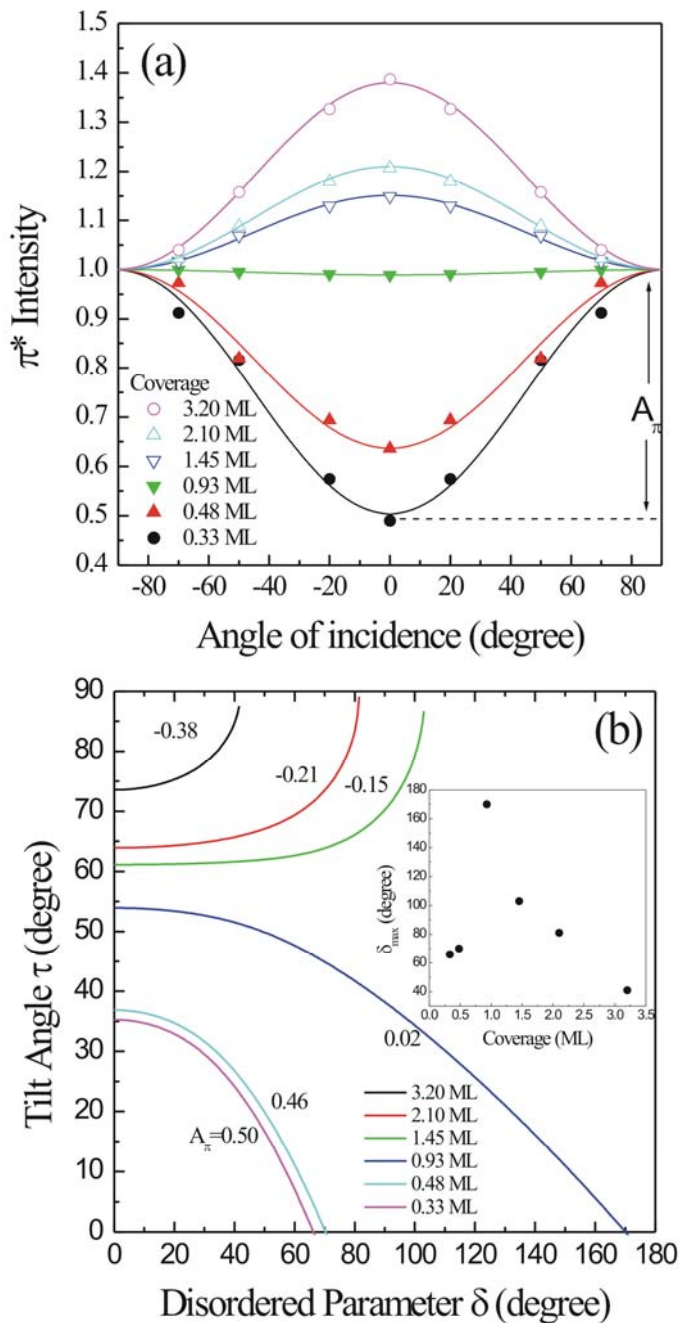
$$P(\omega, \tau, \delta) = G\left(\frac{\omega - \tau}{\delta}\right) / \int_0^{2\pi} d\phi \int_0^{\pi} dx \sin(x) G\left(\frac{x - \tau}{\delta}\right)$$

where  $\omega$  is the polar angle of the  $\pi^*$  orbital vector with respect to the surface normal,  $\delta$  the width of the Gaussian distribution and an orientational disorder parameter,  $\phi$  the azimuthal angle in the surface.

The intensity modulation amplitude,  $A_\pi$ , is defined as  $I(\pi/2, \tau, \delta) - I(0, \tau, \delta)$ , the difference between the intensity for a resonance at grazing incidence angle (90 degrees) and normal incidence (zero degrees). In this model,  $A_\pi$  reflects the molecular orientational order rather than a particular tilt angle.

The intensity of the first  $\pi^*$  absorption resonance as a function of incidence angle at various coverages is shown in Fig.2a. At a first glance, the experimental intensity modulation,  $A_\pi$ , monotonically

decreases from 0.50 to -0.38 with increase of coverage. This indicates that the orientational configuration gradually varies from lying-down ( $A_\pi > 0$ ) to standing-up ( $A_\pi < 0$ ). For each  $A_\pi$ , there is a series of average tilt angle ( $\tau$ ) and orientational disorder parameter ( $\delta$ ) predicted by the model.  $A_\pi$  imposes limits on possible values of  $\tau$  and  $\delta$ . The range of possible  $\delta$  denotes the molecular orientational order.



**Figure 2.** (a) The intensity of the first  $\pi^*$  absorption resonance for CuPc layer at various coverages on Si(111) as a function of incidence angle. The intensity modulation amplitude,  $A_\pi$ , is defined as  $I(\pi/2, \tau, \delta) - I(0, \tau, \delta)$ , the difference between the intensity for a resonance take at grazing incidence angle (90 degree) and normal incidence (zero degree); (b) The solutions of tilt angle ( $\tau$ ) and disorder parameter ( $\delta$ ) for various  $A_\pi$  corresponding to the layers with different coverages. The inset shows  $\delta_{\max}$  representing the molecular orientational order of CuPc layer as a function of coverage.

The solutions for  $\tau$  and  $\delta$  for  $A_\pi$  at various coverages are shown in Fig.2b. It is noted that the values of the tilt angle and the disorder parameter are mutually dependent. However, the maximum of possible value for  $\delta$ ,  $\delta_{\max}$  (which reflects the range of  $\delta$ ) is independent to the value of the tilt angle. The larger the value of  $\delta_{\max}$ , the more disordered the molecular orientation. The parameter  $\delta_{\max}$  as a function of coverage is plotted in the inset of Fig.2b. Below one monolayer,  $\delta_{\max}$  first increases with coverage, suggesting the molecular orientational order of the layer becomes more disordered. At 0.93ML,  $\delta_{\max}$  reaches its maximum at  $170^\circ$ , indicating that the layer is almost completely disordered. Above 1 ML, the molecular orientational order improves with increasing coverage. At 3.20 ML, the narrowest range of  $\delta$  is observed, indicating that a well ordered layer has formed. Assuming  $\delta=0^\circ$  corresponds to the standard analysis adopted by most of XAS measurements, the average tilt angle for this layer is calculated to be  $74^\circ$ , which is consistent with the previous reported tilt angle in thick, well-ordered CuPc/ITO ( $76^\circ$ )<sup>14</sup>, F<sub>16</sub>ZnPc/Mg ( $75^\circ$ )<sup>22</sup>. Hence, at a coverage of 3.20 ML on Si(111), the molecular orientational order is equivalent to that of bulk films several tens of nanometers thick.

The XAS results presented above show that the CuPc film experiences such transitions in which not only the molecular orientation varies from  $\lambda$  to  $\sigma$  structures, but the molecular orientational order also significantly varies with coverage. The interactions, especially molecule-substrate interaction, play an important role in the initial growth of the CuPc film<sup>14</sup>. To understand the phase transitions in the

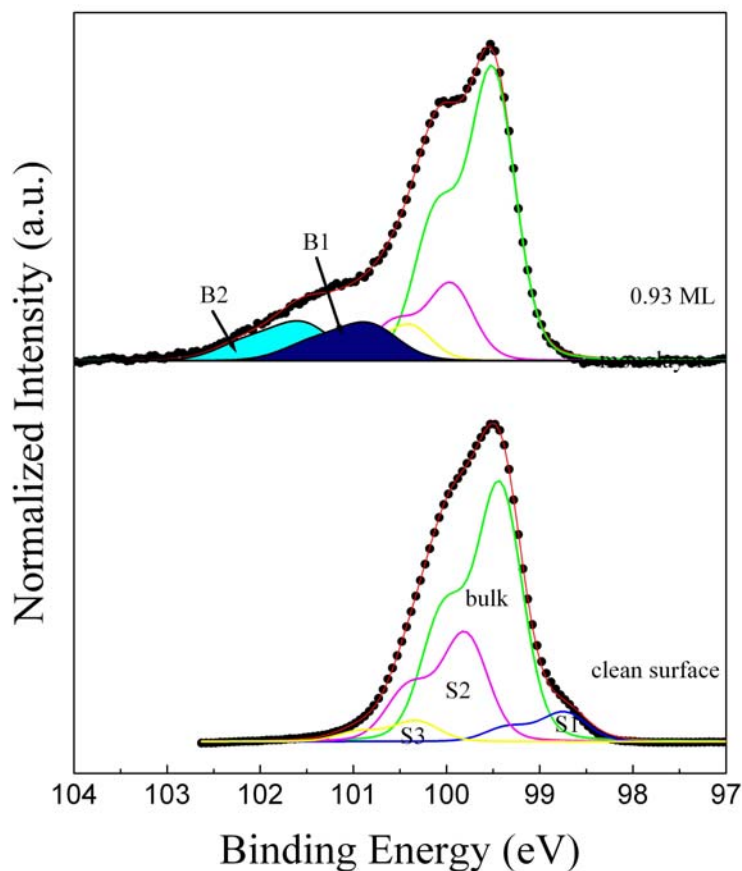


CuPc/Si(111) system, we studied the interactions at a CuPc coverage of one monolayer by core level photoemission spectroscopy, which is a surface sensitive tool for determining the interactions between molecule and surface<sup>23</sup>.

Figure 3 shows the Si 2p core level spectrum acquired with a photon energy of 140 eV at emission angle of 50 degree for clean Si(111)-(7x7) and 0.93 ML CuPc- Si(111). The emission angle is defined as the angle between the electron analyzer for photoemission measurement and the normal direction of the substrate. The Si 2p core level spectrum for the clean Si(111)-(7x7) reconstruction can be well fitted by four Voigt curves, the bulk and three surface core-level shift components, consistent with previous reports<sup>21, 24</sup>. The detailed fitting parameters are adopted from ref.21: Gaussian width of 0.45 eV, Lorentzian width of 0.09 eV, spin-orbit splitting of 0.602 eV and branch ratio of 0.498. The component S1, -0.69 eV relative to the peak position of the bulk component, is attributed to the rest atoms of the (7x7) reconstruction and S2 (+0.37 eV) is attributed to adatom and second layer pedestal atoms. The ratio of the intensities of S1 and S2 is 0.27, within the accepted range (from 0.10<sup>25</sup> to 0.33<sup>26</sup>).

Significant changes are observed in the Si 2p core level spectrum for 0.93 ML CuPc on Si(111). An obvious tail emerges on the high binding side of the spectrum, which indicates the formation of new interactions upon CuPc adsorption. The best fit to this spectrum shows that the component S1 related to the rest atoms has completely vanished and two more components (B1 and B2) emerge at the high binding energy side of the spectrum. Their peak positions relative to that of the bulk component are +1.33 eV and +2.04 eV, respectively. The same fitting parameters as for clean Si are used except for a slightly wider Gaussian width for B1 and B2 (0.76 eV). Compared to the spectra taken at emission angle of zero degree, the Si 2p spectra taken at emission angle of 50 degree are much more surface-sensitive<sup>23</sup>. The intensities of components B1 and B2 on the spectrum taken at emission angle of 50 degree are higher than the counterparts on the spectrum taken at emission angle of zero degree, suggesting the B1 and B2 components are present in the surface of the substrate rather than in the bulk.

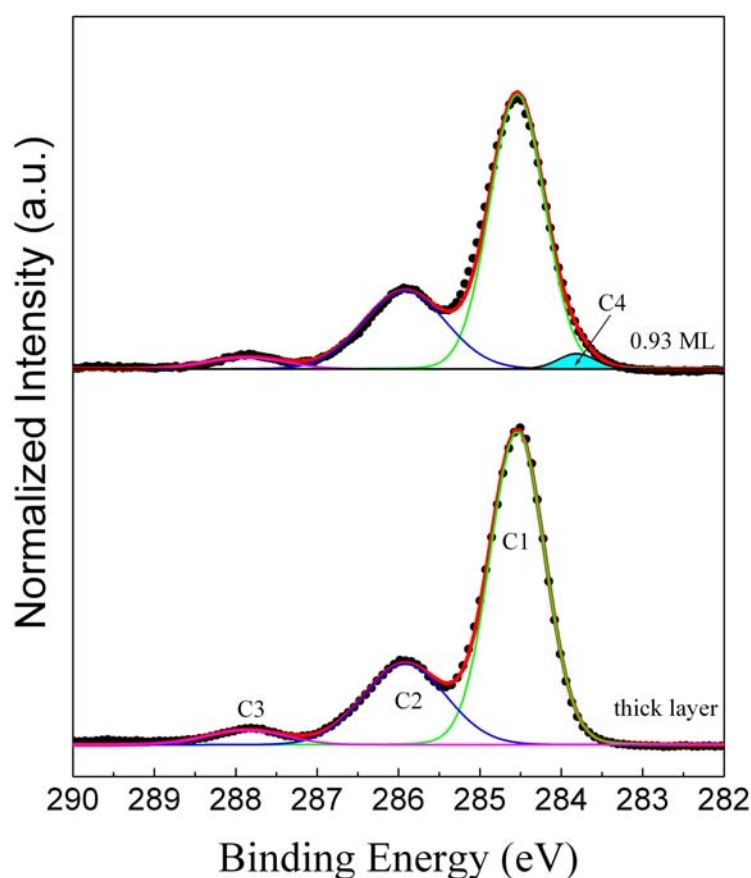
The presence of these two components indicates a strong interaction between the CuPc molecules and the surface.



**Figure 3.** Si 2p core level spectra for clean Si(111)-(7x7), 0.93 ML CuPc/Si(111). The raw data is denoted by black dots and the best fitting curve is plotted as a red solid curve. Fitting components are highlighted as different colors. The spectra presented here are normalized on the main peak intensity.

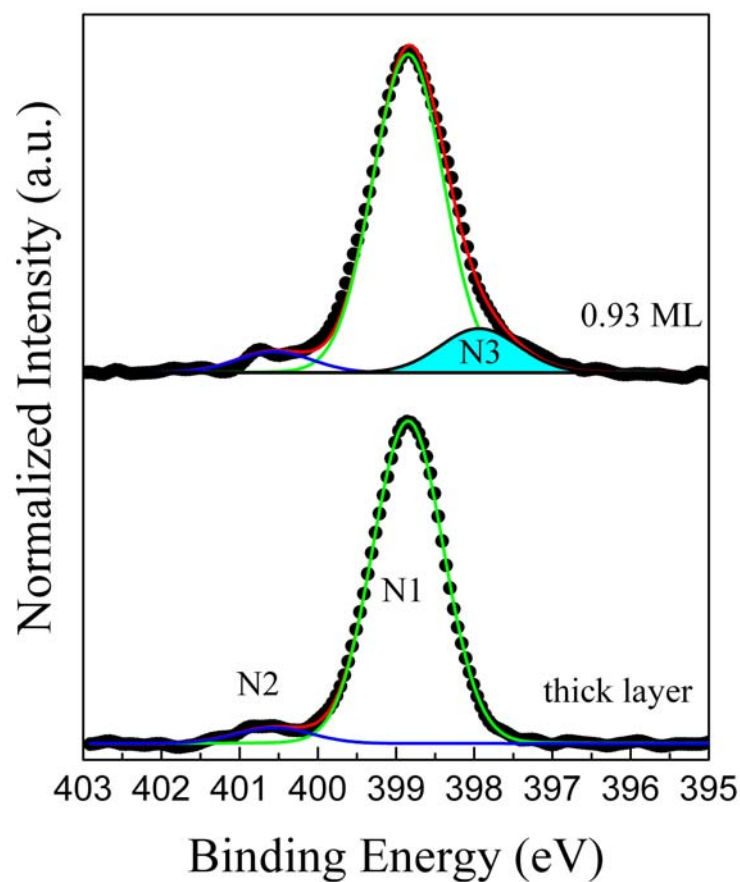
Figure 4 gives the C 1s core level spectra acquired with photon energy of 350 eV at emission angle of zero degree for a thick layer and 0.93 ML of CuPc on Si substrate. The spectrum for a thick layer CuPc represents the case where the interaction between the molecules is dominated by van der Waals forces and  $\pi$ - $\sigma$  interactions. This spectrum is similar to previous reports<sup>27</sup> and can be fitted by three Voigt curves. The components labeled as C1, C2 and C3, are attributed to the carbon atoms of the benzene rings, the pyrolytic carbons linked to nitrogen atoms and a shakeup structure, respectively<sup>27</sup>.

In order to well fit the C 1s core level spectrum for 0.93 ML of CuPc on Si(111), one more component C4 located at the low binding energy side is necessary. During the fitting process, the parameters for the other three components are unchanged. We note that the addition of the C4 component into the fitting is not unique, but is an indicator of the presence of the interaction between the carbon atoms and the Si atoms since the electronegativity of C is higher than that for Si<sup>23</sup>. This is consistent with the emergence of two components at the higher binding side of Si 2p core level spectrum in Fig. 3, and reveals that there is a strong interaction between the carbon atoms of adsorbed CuPc molecules and the Si substrate.



**Figure 4.** C 1s core level spectra for a thick layer and 0.93 ML CuPc/Si(111). The raw data is denoted by black dots and the best fitting curve is plotted as a red solid curve. The fitting components are highlighted as different colors. The spectra presented here are normalized on the main peak intensity.

Figure 5 shows the N 1s core level spectra acquired with photon energy of 450 eV at emission angle of zero degree for a thick layer and 0.93 ML of CuPc on Si substrate. The spectrum for the thick layer of CuPc is consistent with a previous report<sup>27</sup> and is characterized by a single peak at 398.8 eV (N1) followed by a shakeup feature at higher binding energy (+1.8 eV). One additional component (N3) emerges at the lower binding energy side (-0.9 eV) of the N 1s core level spectrum for one monolayer CuPc on Si(111). Dofour et al. reported an intense satellite at higher binding energy (about +5.1 eV from the main peak), due to poorly screened final state effects, in the N 1s spectrum after adsorption of CuPc on Si(111), and they suggested that there is weak coupling between the nitrogen atoms of CuPc molecules and silicon<sup>27</sup>. In our study, no such satellite peak is observed and a component (N3) related to the strong interaction between the nitrogen atoms and the Si surface is clearly detected. This suggests that the nitrogen atoms of the CuPc molecule are strongly coupled to the Si surface.



**Figure 5.** N 1s core level spectra for a thick layer and 0.93 ML CuPc/Si(111). The raw data is denoted by black dots and the best fitting curve is plotted as a red solid curve. The fitting components are highlighted as different colors. The spectra presented here are normalized on the main peak intensity.

The core level Si 2p, C 1s and N 1s spectra presented above demonstrate that there is a strong interaction between the adsorbed CuPc molecules and the Si(111) surface. This interaction between the molecules and surface is not appropriately described as Si-C and Si-N bonding and the  $\pi$ -electrons of the molecules might be also involved. We note that not only the carbon atoms in the benzene rings but also the nitrogen atoms can be directly coupled to the Si surface. To realize the coupling between the nitrogen atoms of the molecules and the surface, the CuPc molecules have to adopt a lying-down geometry ( $\lambda$  structure). At the early stage of CuPc growth on Si(111), there is enough space for the molecules to adopt the lying-down geometry, as observed in the XAS measurement for 0.33 ML CuPc (Fig.1a). The previous scanning tunneling microscopy study on the adsorption of CuPc on Si(111) shows that the molecules appear as completely flat planes on the surface<sup>18,19</sup>. With increase in coverage, additional molecules experience increasing difficulty of adopting lying-down positions due to steric hindrance of neighboring adsorbed molecules, but are still coupled to the surface. Hence, the adsorption geometry becomes more disordered. This shows in the XAS spectra as independence of the absorption intensity on the incident angle (Fig.1b).

A standing molecular orientation of CuPc was observed on very rough surfaces<sup>14</sup>. When the surface roughness is larger than the molecular size, the standing adsorption geometry ( $\sigma$  structure) is favorable due to the weakened interaction between the molecules and the substrate<sup>28</sup>. After the whole Si surface is passivated by one monolayer of molecules, the substrate is well screened. The  $\pi$ - $\sigma$  molecule-molecule interaction, which tends to organize the molecules in herringbone structure, is larger than the molecule-substrate interaction. Therefore, only the  $\sigma$  structure is favorable in the subsequent multilayer growth of CuPc film after one monolayer coverage. Moreover, the molecular orientational order for  $\sigma$

structure is significantly improved with increasing coverage, as shown in Fig.2b. This self-ordering is driven by the intermolecular interaction of CuPc molecules, mainly the  $\pi$ - $\sigma$  interaction between the rings of the molecules. We note that the layer at 3.20 ML coverage is as ordered as several-tens-of-nanometers thick bulk-like film. This suggests that high quality ordered CuPc films can be achieved at several-monolayer coverage.

#### **4. Conclusion**

We have studied *in situ* the molecular orientation and order at the initial stage of CuPc growth on Si (111)-(7x7) by angular-dependent XAS and PES. A transition from  $\lambda$  structure to  $\sigma$  structure occurs when the coverage is less than one monolayer. After the Si surface is completely passivated by the molecules, only the  $\sigma$  structure forms during further growth. The transition of molecular orientation is related to the changes in the interactions from molecule-substrate covalent interactions to intermolecular interactions. During the first monolayer growth, the film also experiences a transition in which the molecular orientational order exhibits order-disorder-order behavior. At several-monolayer coverage, a well ordered organic molecular layer is achieved.

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