ABSTRACT: The structural order of C₆₀ thin films is shown to be significantly improved by inserting a templating layer of diindenoperylene (DIP) between the SiO₂ substrate and C₆₀. In contrast to growth on an amorphous substrate like SiO₂, C₆₀ grown on DIP exhibits alignment of fcc-domains with the (111) plane parallel to the substrate and a significant increase of the coherent in-plane island size by a factor of ∼4. Modification of the structural quality of the DIP bottom layer leads to a change in structural order in the C₆₀ top layer. In addition, ultraviolet photoelectron spectroscopy data from templated and nontemplated C₆₀ films are discussed. In contrast to other anisotropic organic molecules, for C₆₀ the spectral broadening and density of states of the highest occupied molecular orbital region do not depend significantly on the structural order in the C₆₀ film, which can be rationalized by the isotropic shape of the C₆₀ molecule.

INTRODUCTION

For growth of organic thin films the structure and morphology depends strongly on the substrate onto which they are deposited.¹,² This was demonstrated, for example, by the surface modification of an inorganic substrate with an organic self-assembled monolayer (SAM), which influenced the resulting growth behavior.³⁻⁴ For such heterostructures the growth behavior of the top layer is mostly discussed in terms of surface energies, although also some degree of azimuthal alignment has been observed.⁵⁻⁶ In contrast, a close relationship between two organic layers can be observed in organic–organic heteroepitaxy.⁷⁻¹⁵ There, the growth behavior of the deposited compound depends on the, usually anisotropic, potential surface of both involved materials. The control of the top layer morphology by tuning of the bottom layer was also discussed as templating, particularly for changing the molecular orientation relative to the surface (standing orientation vs lying orientation).¹⁶⁻¹⁷

The structural relationship at an organic–organic heterointerface resulting from the nonequilibrium growth process has a large impact on electrical properties, inter alia charge carrier generation, and transport.¹⁸⁻¹⁹ For example, for organic field effect transistors it was shown that an organic templating layer may improve the electronic mobility of the active material substantially.²⁰⁻²² In this regard, an important point for small-molecule organic semiconductors can be the orientation of the molecules. Frequently, there is at least a competition between lying down and standing up orientation,²³⁻²⁵ which depends strongly on the underlying substrate. Other systems, such as PTCDA, exhibit a very strong tendency to form lying-down structures, almost independent of the substrate.²⁶⁻²⁷ In this context, C₆₀ is a rather unique case in the area of small-molecule organic semiconductors, since it exhibits essentially rotational symmetry. The issue of lying-down vs standing-up orientation does not complicate matters, and the orientational degrees of freedom in structure formation enter basically only via the orientation of the lattice planes and their distribution or alignment. C₆₀ was shown to grow with low structural order on several inorganic substrates like SiO₂,²⁸ quartz glass,²⁹ and sapphire³⁰ but crystallizes well on organics like pentacene,³¹⁻³³ or sexiphenyl.³⁴⁻³⁵

In this paper we study the influence of a diindenoperylene (DIP) Figure 1) templating layer, on the growth and electronic structure of C₆₀. The combination of C₆₀ and DIP in a heterostructure was shown to exhibit excellent photovoltaic performance,³⁶⁻³⁹ which is related to the high exciton diffusion length in DIP,⁴⁰⁻⁴¹ and the favorable energy level alignment of both materials.³⁸⁻³⁹ In addition, we investigate to which extent structural properties like roughness, domain size, and
crystallinity of the DIP templating layer influence the growth of C_{60}.

### EXPERIMENTAL SECTION

Organic thin films were deposited on silicon wafers with native SiO$_2$ (surface roughness $\sigma_{rms} = 0.3$ nm) under ultra high vacuum (UHV) conditions (base pressure $< 6 \times 10^{-7}$ Pa) by thermal evaporation. Before deposition, substrates were cleaned ultrasonically with acetone, isopropyl alcohol, and ultra pure water, followed by heating to 700 K in the UHV growth chamber. The growth rate was between 0.1 and 0.3 nm/min in water, followed by heating to 700 K in the UHV preparation chamber. The samples were directly transferred to the measurement chamber without breaking the vacuum. The vacuum level (VL) was obtained by applying a sample bias of $-5$ V during the UPS measurements.

### RESULTS

**X-ray Scattering.** To study the structure of C$_{60}$ thin films we compare first a reciprocal space map of a C$_{60}$ film grown on SiO$_2$ (C$_{60}$/SiO$_2$; Figure 2a) with data from C$_{60}$ grown on DIP (C$_{60}$/DIP; Figure 2b). The C$_{60}$/SiO$_2$ film exhibits broad diffraction rings indicating crystalline domains without preferred orientation. Indexing is done according to the C$_{60}$ fcc structure reported in ref 48. One reflection, indexed as C$_{60}$# in the bottom GIXD data, does not stem from the C$_{60}$ fcc structure. Its q-value ($q = 0.725$ Å$^{-1}$) coincides with the (100) reflection from the C$_{60}$ hcp structure. This observation is in agreement with single crystal growth, where a small fraction of crystals adopt hcp packing. Note that in the indexing of GIXD data at the bottom of Figure 2a only one index for each reflection is given, since other reflections with the same q, cannot be distinguished. The scattering data of the C$_{60}$/SiO$_2$ film shown here are in agreement with data presented in ref 28.

Figure 2b displays 2-dimensional GIXD data from a C$_{60}$/DIP heterostructure. At the bottom the integrated GIXD intensity is shown. Indexing is done again according to the C$_{60}$ fcc structure. Compared to C$_{60}$ grown on SiO$_2$ (Figure 2a) the diffraction pattern of C$_{60}$ grown on DIP shows significant differences. The distribution of Bragg reflections reveals the alignment of the fcc-(111) crystal plane parallel to the substrate. Only a small fraction of crystallites nucleates with a random orientation as indicated by the weak C$_{60}$ (111)* index. Note that the Bragg reflection at $q_{111} = 0.725$ Å$^{-1}$ stems not from the hcp structure as in Figure 2a. Instead, this peak is the projection...
of the fcc(11−1) Bragg reflection onto the \( q_{xy} \) plane. The width of the fcc Bragg reflections in \( q_{zz} \) (out-of-plane) is relatively large because of the small crystal size in the \( q_{zz} \) direction limited by the film thickness of 15 nm. The in-plane coherent crystal sizes \( l_{\parallel} \) of both \( C_{60} \) films were determined with the Scherrer formula to be \( l_{\parallel} = 7 \) nm for the \( C_{60}/SiO_2 \) film and \( l_{\parallel} = 28 \) nm for the \( C_{60}/DIP \) film. For the determination of \( l_{\parallel} \) of both \( C_{60} \) films we choose the (2−20) and (4−2−2) reflections and averaged over the obtained values. The difference in \( l_{\parallel} \) is clear evidence for the improved crystal quality and reduction of crystal defect density in the \( C_{60}/DIP \) film compared to the \( C_{60}/SiO_2 \) film.

Complementary XRR data are shown in Figure 3. Here, the templated \( C_{60}/DIP \) film exhibits two pronounced Bragg reflections, indexed (111) and (222). However, no Bragg reflection is observed for the \( C_{60}/SiO_2 \) film. The root-mean-squared roughness \( \sigma_{rms} \) determined from the Kiessig-fringes near the total reflection edge is \( \sigma_{rms} = 3.0 \pm 0.3 \) nm for both \( C_{60} \) films, indicating that the roughening in this thickness region (~15 nm) does not strongly depend on the templating effect. The XRR data confirm the enhanced crystal quality and orientational ordering of \( C_{60} \) on DIP in comparison to \( C_{60} \) grown on SiO\(_2\).

Figure 4 summarizes the difference of the structure of the \( C_{60}/SiO_2 \) and \( C_{60}/DIP \) films. In the \( C_{60}/SiO_2 \) film grains are small and have no preferred orientation. In contrast, coherently ordered domains in the \( C_{60}/DIP \) film are larger and oriented with the (111) plane parallel to the surface.

For a more detailed understanding of the observed templating effect we test if the structural quality or the roughness of the templating layer influences the \( C_{60} \) growth. The growth of DIP on SiO\(_2\) is already well established for different thicknesses and temperatures.\(^{34,36,49}\) DIP films are predominantly textured with the (001) plane (DIP HT phase) parallel to the substrate, which corresponds to roughly standing molecules. In the thickness region below ~10 nm, DIP exhibits layer-by-layer growth with a metastable DIP structure\(^{36,50}\) followed by rapid roughening for thicker films.\(^{34}\) Generally, films grown at elevated substrate temperatures are of higher crystal quality compared to low temperature deposited films.\(^{17,49}\)

Figure 5a shows GIXD data of 15 nm \( C_{60} \) films grown on DIP films with different thicknesses and on bare SiO\(_2\).

### Table 1. Summary of DIP templating layers

<table>
<thead>
<tr>
<th>Thickness (( d ))</th>
<th>( \sigma_{rms} ) deposition temperature (( T ))</th>
</tr>
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<tbody>
<tr>
<td>~15 nm</td>
<td>( T = 300 ) K</td>
</tr>
<tr>
<td>~35 nm</td>
<td>( T = 380 ) K</td>
</tr>
<tr>
<td>~55 nm</td>
<td>( T = 450 ) K</td>
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Thicknesses \( d \), \( \sigma_{rms} \) and deposition temperatures \( T \) of the DIP templating layers are summarized in Table 1. Clearly the peak width and intensity of the \( C_{60} \) reflections vary for different DIP bottom layers. As an indicator for structural quality for the obtained films, we use the coherent in-plane island size \( l_{\parallel} \) evaluated with the Scherrer formula. Figure 5b shows the correlation between \( l_{\parallel} \) of the \( C_{60} \) film with the DIP film thickness. As already shown, the crystal quality of the \( C_{60} \) film is enhanced strongly \( (l_{\parallel} \text{ increase by a factor of } \sim 4) \) by already ~2–3 monolayers of DIP. For thicker templating layers the \( l_{\parallel} \) of the \( C_{60} \) film is roughly constant for DIP thicknesses of at least up to 55 nm. We determined \( \sigma_{rms} \) of the three DIP templating layers (Table 1) from reflectivity data (not shown). The obtained roughness values are in agreement with the rapid roughening observed for DIP.\(^{34}\) The increasing \( \sigma_{rms} \) for thick templating layers seem to have no effect on the \( C_{60} \) coherent in-
plane island size, which stays nearly constant in the studied thickness region (Figure 5b).

To further examine if a decrease in crystallinity in the DIP bottom layer affects the crystal quality of the C₆₀ film, we tuned the structure of the DIP templating layer by the substrate temperature during growth. Figure 6a shows GIXD data of 15 nm C₆₀ films grown on DIP films (d ≈ 15 nm) prepared at T = 200, 300, and 380 K. All three templating layers consist predominantly of textured DIP HT phase domains; however, ls of DIP is significantly reduced at lower T, which was also demonstrated in refs 17 and 49. Figure 6b compares the ls of C₆₀ films with the ls of the underlying DIP films determined from the GIXD data in part a. For the determination of ls of DIP and C₆₀ films we averaged the obtained values from several Bragg reflections.

Overall shape of the HOMO and HOMO-I states in Figure 7a corresponds to spectra measured for C₆₀ thin films on various inorganic and organic substrates/films. The similarity to the gas phase spectra of C₆₀ indicates only weak interaction between molecules in the thin film. Apart from a spectral shift of 150 meV, resulting from the different energy level alignment (ELA) of the C₆₀ film to the DIP layer and the SiO₂ substrate, both spectra from the C₆₀ films are essentially identical. This can be seen more clearly in the inset in Figure 7a, where the data are overlaid and the C₆₀/DIP data were shifted by 150 meV. In addition, also the ionization potentials (IP) determined by the secondary electron cutoff and the HOMO onset are equal (6.4 eV) for both C₆₀ films. Strong changes in overall shape of the HOMO and HOMO-I states in Figure 7a corresponds to spectra measured for C₆₀ thin films on various inorganic and organic substrates/films. The similarity to the gas phase spectra of C₆₀ indicates only weak interaction between molecules in the thin film.
structure and domain orientation for organic thin films lead to a significant change in spectral width of the HOMO or the IP depending on the molecular system. However, our data demonstrate that at room temperature thin films of C60 do not show these effects because of the reasons described below.

In general several mechanisms may influence the HOMO bandwidth of a molecular material. For instance, in a nonuniform or disordered film the polarization energy (final state effect) and the intermolecular interaction (initial state effect) are locally different, resulting in slightly different ionization energies at different positions and therefore in spectral broadening. Another broadening effect is associated with band dispersion due to delocalization of the electronic states, which can be observed only for large single crystals of C60 and can therefore be omitted in the following discussion.

In comparison to the C60/SiO2 film we may expect spectral sharpening for the C60/DIP film, because of the improved crystal quality. The island size of the C60/SiO2 film is much smaller compared to that of the C60/DIP film, implying that the density of crystal defects is higher in the C60/SiO2 film compared to the C60-on-DIP film. However, the absence of any difference in the width of the C60 states implies that a small coherent island size in a C60 film has no significant impact on the polarization energy/intermolecular interaction. This observation may be rationalized by the high-symmetry shape of the polarization energy/intermolecular interaction. This observation may be rationalized by the high-symmetry shape of the molecular material. For instance, in a organic heterostructures the ELA of the top layer is different, resulting in slightly different Fermi level leading to an interface dipole of 0.36 eV. For the mechanisms of energy level alignment at the organic–inorganic and organic–organic interfaces several different models have been discussed without a definitive conclusion in the literature. Figure 7b summarizes the ELA of two measured samples. For a low work function substrate like SiO2 (WF = 4.23 eV) the C60 LUMO (lowest unoccupied molecular orbital) level is presumably located at the substrate Fermi level leading to an interface dipole of 0.36 eV. For organic–organic heterostructures the ELA of the top layer is typically governed by the energetic position of the bottom layer. The difference of the HOMO onsets of DIP and C60 as determined here is ΔE_{HOMO} = 0.86 eV, similar to values reported for a DIP/C60 heterostructure on PEDOT:PSS and for the vice versa heterostructure (DIP-on-C60).

### SUMMARY

In summary, we demonstrated that the structural order of C60 is significantly improved by inserting a DIP templating layer between the SiO2 substrate and C60 film. In contrast to growth on an amorphous substrate like SiO2, C60 grown on a DIP film exhibits alignment of fcc domains with the (111) plane parallel to the substrate and a significant increase of the coherent in-plane island size (l_2) by a factor of ~4. In addition, it was shown that an increase in structural order of the DIP templating layer leads to a similar increase of structural order in the C60 top layer. UPS measurements revealed that the spectral broadening of the C60 HOMO region interestingly do not depend significantly on the structural order in the C60 film. This observation can be rationalized by the highly symmetric shape of the C60 molecule.

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