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Citation: AIP Advances 5, 117241 (2015); doi: 10.1063/1.4936884
View online: http://dx.doi.org/10.1063/1.4936884
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(Received 8 September 2015; accepted 16 November 2015; published online 30 November 2015)

Highly crystalline and stable molecular superlattices are grown with the smallest possible stacking period using monolayers (MLs) of the organic semiconductors pentacene (PEN) and perfluoro-pentacene (PFP). Superlattice reflections in X-ray reflectivity and their energy dependence in resonant soft X-ray reflectivity measurements show that PFP and PEN MLs indeed alternate even though the coherent ordering is lost after ∼ 4 ML. The observed lattice spacing of 15.9 Å in the superlattice is larger than in pure PEN and PFP films, presumably because of more upright standing molecules and lack of interdigitation between the incommensurate crystalline PEN and PFP layers. The findings are important for the development of novel organic quantum optoelectronic devices.

INTRODUCTION

Superlattices and quantum wells are widely used in inorganic semiconductor devices, for example to tailor the electronic structure, tune the emission wavelength, and lower stimulated emission thresholds. Organic, molecular semiconductors have meanwhile proven to be versatile materials for a wide range of (opto-) electronic applications such as commercially available organic light-emitting diodes (OLEDs), thin film transistors and organic photovoltaic cells. Despite significant efforts to tune the nanoscale morphology of molecular heterostructures, only a few examples of organic superlattices exist in literature. There have been demonstrations of organic multilayer photodetectors with superior efficiency and bandwidth, vertical superlattices have been produced for solar cells, and organic quantum wells have been shown to exhibit quantum confinement effects. Also, hybrid organic-inorganic quantum well structures have been demonstrated for excitonic energy transfer, and negative differential resistance based on resonant tunneling has been realized in crystalline organic quantum wells, which may lead to the realization of new functionality in novel organic “quantum” optoelectronic devices.

The challenging growth procedures needed to achieve the necessary high structural and sub-nm precision in molecular assemblies with sub-nm precision have been addressed in several studies using organic molecular beam deposition (OMBD). In early work, organic semiconductor multiple quantum wells or superlattices with stacking periods of a few molecular monolayers (MLs) and up to several nm have been studied with X-ray diffraction, RHEED, and SIMS, as well as imaged with TEM. It has been found that in contrast to inorganic superlattices where lattice matching is a prerequisite, the weaker van der Waals bonds in molecular materials allow for crystalline layers even in stacks of incommensurate lattices. More recently, deposition methods such as hot-wall deposition...
FIG. 1. a) Chemical structure of pentacene (PEN). b) Chemical structure of perfluoro-pentacene (PFP). c) AFM height image of a superlattice of 10 alternating monolayers of PFP and PEN.

have been used to grow smooth layers,\textsuperscript{12} and weak epitaxy growth has resulted in highly crystalline superlattices.\textsuperscript{13} Not all of the referenced superlattice structures consist of thin enough layers to allow for significant coupling of electronic states between neighboring potential wells and therefore do not achieve true electronic superlattice states; here we presume the formation of a superlattice from an atomic/molecular structure perspective only.

The materials used here, pentacene (PEN, Figure 1(a) and perfluoro-pentacene (PFP, Figure 1(b), are popular organic semiconductors; PEN is used for p-type transistors and biosensor applications due to its good charge carrier mobility,\textsuperscript{14} while PFP also exhibits good mobility and has been used as n-type transistors in complementary circuits with PEN.\textsuperscript{15} Both molecules exhibit high structural order and a well-defined growth mode in pure PEN films\textsuperscript{16–19} and pure PFP films.\textsuperscript{20–22} The two compounds have been shown to form a 1:1 co-crystal with strong charge transfer and excitonic coupling,\textsuperscript{23} but PEN and PFP crystals are not continuously miscible.\textsuperscript{24,25}

In this paper, we show that stable organic superlattice structures consisting of alternating pentacene (PEN) and perfluoro-pentacene (PFP) monolayers are formed using OMBD with \textit{in situ} and real-time X-ray thickness monitoring. We use x-ray reflectivity and resonant soft X-ray reflectivity\textsuperscript{26} to measure superlattice reflections proving that PEN and PFP MLs alternate. We further find that the out-of-plane lattice constant of 15.9 Å is larger than in pure PEN (15.4 Å) and pure PFP (15.7 Å) thin films; the origin of this increase is attributed to more upright standing molecules and non-interdigitating layers of the incommensurate PFP and PEN crystal lattices.

EXPERIMENTAL

The superlattice of PFP (Figure 1(a), Kanto Denka Kogyo Co., 99%) and PEN (Figure 1(b), Sigma-Aldrich, 99.9%) was grown using OMBD in high vacuum conditions at a base pressure of $p = 1 \times 10^{-9}$ mbar.\textsuperscript{27} We changed back and forth five times between PFP and PEN evaporation at a rate of $\sim 1$ Å/min onto silicon oxide substrates held at a temperature of 30 °C. For the first MLs, we used \textit{in situ} X-ray reflectivity, which oscillates with a period of two MLs, to determine the exact moment each PEN or PFP ML ($\sim 16$ Å) was closed.\textsuperscript{28} Prior to growth, the silicon substrates with native oxide (thickness $\sim 10$ Å) were cleaned by sonication in acetone and isopropanol, a rinse with ultrapure water, followed by heating to 400 °C in vacuum.
In situ measurements of the film thickness and out-of-plane lattice spacing were performed using X-ray reflectivity (XRR) with Cu Kα radiation. Resonant soft X-ray reflectivity at the fluorine edge (~690 eV) was performed at the Advanced Light Source (ALS, Berkeley) at beamline 6.3.2. The thin film crystal structure was determined using grazing incidence X-ray diffraction (GIXD) with Cu Kα radiation on a laboratory diffractometer, while GIXD maps with a 2D detector were acquired at the ALS beamline 7.3.3 at an energy of 10 keV. Lastly, the surface morphology was imaged using a Veeco MultiMode atomic force microscope (AFM) in non-contact mode.

RESULTS

The morphology of the stack of five PFP/PEN bilayers is shown in Figure 1(c). Several large crystallites with a height of more than 100 nm are visible on top of a smoother superlattice film consisting of islands and trenches in the 10 nm height range. Elongated islands resemble the shape of islands in PFP films, but there are also more compact islands as in PEN thin films. On top of some islands, molecular step edges with a height of ~15 Å can be discerned, which points to upright standing PEN and PFP molecules.

For a more quantitative measurement of the out-of-plane lattice constant and to check whether PFP and PEN layers alternate, we performed XRR measurements as shown in Figure 2(a). In the low q-range, Kiessig oscillations are visible from which the total film thickness can be determined.

![Graph](image-url)
with a Parratt fit to be 180 Å with a roughness of 30 Å. Bragg reflections up to 4th order are visible, demonstrating the high structural order of the thin film. Interestingly, the out-of-plane lattice constant derived from the Bragg reflections is 15.9 Å, which is larger than the out-of-plane lattice constants of PEN (c* = 15.4 Å) as well as PFP (a* = 15.7 Å). At q-values of $1/2 q_{\text{Bragg}} = 0.198 \text{ Å}^{-1}$ and $3/2 q_{\text{Bragg}} = 0.296 \text{ Å}^{-1}$, additional superlattice reflections are visible due to the differences in density as well as scattering length density (SLD) between PFP (2.2 g/cm$^3$, SLD = 18.3 Å$^{-2}$ at 8.0 keV) and PEN (1.3 g/cm$^3$, SLD = 11.8 Å$^{-2}$ at 8.0 keV). These two reflections correspond to a periodicity of 32 Å and prove without doubt that through exact control of alternating PFP and PEN MLs during growth, a new superlattice periodicity different from the 15.9 Å layering is achieved. These bilayer superlattice reflections are wider than the ML periodicity Bragg reflections though, indicating that the superlattice is only coherently ordered over 70 Å, corresponding to the first four MLs.

To prove further that the fluorine atoms and, therefore, the layers of PFP molecules alternate with PEN, we acquired resonant soft X-ray reflectivity as shown in Figure 2. Soft XRR below the fluorine absorption edge at 670 eV does not show a superlattice reflection, while for XRR at 689.7 eV the superlattice reflection at $q = 0.19 \text{ Å}^{-1}$ is visible. The energy of 670 eV, well below the fluorine K-edge, which is at a nominal value of 697 eV, was chosen as the reference point, while the resonant scattering at $q = 0.19 \text{ Å}^{-1}$ is enhanced the most at 689.7 eV, as can be seen from the inset of Fig. 2(b). This energy dependent reflectivity at fixed $q$ shows the effects of enhanced scattering and absorption at the fluorine edge, albeit not at the nominal K-edge value of 697 eV but shifted to 689.7 eV and 696.0 eV. The intensities of the double peak reflect the ratio of four fluorine atoms in corner positions and the ten fluorine atoms in the edge positions, with their distinct bonding environment. However, unoccupied molecular orbitals also play a role in the shape and positions of the peaks. The $q_z$-dependent measurements at different energies in Fig. 2(b) in principle allow for a quantification of the layering of fluorine atoms, but the large scattering angles of up to 180$^\circ$ and the presently unknown anisotropic soft X-ray absorption of the anisotropic PFP molecule prevent a quantitative fit. Qualitatively, the interactions between PFP and PEN with 670 eV X-rays are similar, leading to a lack of a superlattice reflection and a strong Bragg reflection at 670 eV. At 689.7 eV, the X-rays interact more strongly with PFP than PEN so that those PFP layers lead to a superlattice reflection and a weaker but unshifted Bragg reflection. This dependence of the superlattice reflection on the scattering from fluorine atoms clearly shows that PFP and PEN MLs alternate.

To complement the information on the out-of-plane structure, GIXD data was acquired both with a 2D detector (Figure 3(a)) and a point detector scan (Figure 3(b)). The positions of in-plane reflections of the point detector scan in Figure 3(b) agree very well with the known structures of pure PFP$^{21}$ and PEN$^{16}$ thin films as indicated in Table I. The asymmetry and width of the GIXD Bragg reflections are too large to be able to distinguish between the monolayer and thin film phases of PEN (see Table I). At the positions of mixed phase reflections (from reference,$^{24}$ see arrows in Figure 3(b), no significant Bragg reflection intensities are found, indicating that no PEN-PFP co-crystal is formed. In the reciprocal space map in Figure 3(a), PFP and PEN Bragg rods with higher order reflections in $q_z$ are present, which indicate crystalline multilayer domains consisting of pure PFP or pure PEN, respectively. This could be partially due to textured crystallites on top of the film as well as single phase regions within the film where the alternating PFP - PEN stacking is lost.

In summary, the structure of the 180 Å thick PFP – PEN superlattice is characterized by the following observations, depicted in the simplified schematic of Figure 4. The 180 Å thick film has a surface roughness of ∼30 Å and some large crystallites form on top (not depicted in Fig 4). The crystal structure within the molecular film surprisingly exhibits an out-of-plane lattice constant of 15.9 Å that is larger than both the 15.4 Å spacing of PEN and the 15.7 Å spacing of PFP multilayer films. This can be explained by several factors. In a single PEN ML, the 16 Å long molecules have been found to stand upright at exactly 90$^\circ$ in contrast to PEN molecules in multilayers, which are slightly tilted at 95.1$^\circ$. Therefore, we propose that a single PEN layer enclosed by PFP MLs is standing upright, consistent with the measured lattice constant. PFP within the superlattice can also be less tilted, but a second contribution to the larger PFP lattice constant is due to the interdigitation of successive molecular layers. In a PFP crystal, the adjacent ML interdigitates by ∼1.6 Å, but this interdigitation is reduced at a PFP - PEN interface due to their incommensurate in-plane unit cells (see Figure 4). Therefore, the effective thickness of single PFP layers is increased in comparison to
a pure PFP crystal. Hard XRR and soft resonant XRR show that a superlattice is formed; however, the coherently ordered thickness of \( \sim 70 \) Å observed in XRR means that the ordering extends only for about four to five MLs within the 180 Å thick film. PFP only grows in a layer by layer fashion for 1 – 2 MLs\(^{20}\) and PEN for less than 4 MLs on top of silica.\(^{30}\) Beyond this thickness, surface roughening leads to holes in PEN layers that get filled with PFP and vice versa, reducing the structural definition of the superlattice. Using molecules that exhibit a more pronounced layer-by-layer growth such as DIP, PTCDD-C8 or C60 would enable an extended superlattice with more periods. Increasing the substrate temperature for PFP/PEN growth also leads to smoother films and therefore could improve the superlattice. However at elevated substrate temperatures, intermixing of PFP and PEN layers and formation of co-crystals occurs,\(^{25}\) which is counterproductive.

In our superlattice, no intermixing of the two molecular species in a mixed phase co-crystal is found in GIXD, despite the proximity of alternating MLs of both compounds. Further, the superlattice has been found to be stable on timescales of at least one year. These findings are consistent with observations that both bilayers as well as multilayers of PFP and PEN mix at elevated substrate temperatures of 60 °C during growth but not during annealing, when the structure is already formed.\(^{25}\)

A key factor of this desirable property is that blends of PFP and PEN cannot have arbitrary mixing

\[\text{TABLE I. Positions of in plane Bragg reflections for a PEN ML, PEN thin films and PFP thin films.}\]

|                | PFP (002) | PEN (110) | PFP (011) | PEN (200) | PFP (012) | PEN (210) |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Superlattice   | 1.10(5) Å\(^{-1}\) | 1.34(7) Å\(^{-1}\) | 1.49(5) Å\(^{-1}\) | 1.67(4) Å\(^{-1}\) | 1.77(7) Å\(^{-1}\) | 1.96(3) Å\(^{-1}\) |
| PEN ML\(^{31}\) | 1.346 Å\(^{-1}\) | 1.656 Å\(^{-1}\) | 1.967 Å\(^{-1}\) |
| PEN thin film\(^{16}\) | 1.338 Å\(^{-1}\) | 1.654 Å\(^{-1}\) | 1.959 Å\(^{-1}\) |
| Pure PFP\(^{20,21}\) | 1.10 Å\(^{-1}\) | 1.49 Å\(^{-1}\) | 1.77 Å\(^{-1}\) |
CONCLUSIONS

We have demonstrated the growth of a highly crystalline PEN - PFP superlattice with the smallest possible period of individual molecular MLs. The lattice constant differs from both individual materials due to molecular tilt changes and lack of interdigitation between incommensurate PEN and PFP lattices. Future improvements in molecular layer-by-layer growth would allow for more perfect repetitions in the superlattice stacking. The ability to grow this material class of engineered organic semiconductor thin films opens new possibilities for organic “quantum” devices and can enable tailored excitonic and electronic coupling.

ACKNOWLEDGEMENTS

We would like to acknowledge help from T. Hosokai, H. Frank, N. Llóbera, and discussions with I. Salzmann. SK acknowledges funding from the German research foundation (DFG via SFB 951). SRL acknowledges the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division through Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231.

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