

Structure of *p*-Sexiphenyl Nanocrystallites in ZnO Revealed by High-Resolution Transmission Electron Microscopy

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Supporting Information

ABSTRACT: The structure of *para*-sexiphenyl (6P) nanocrystallites embedded in ZnO single crystals is resolved by cross-sectional high-resolution transmission electron microscopy (HRTEM) combined with image contrast simulations and X-ray diffraction measurements. The hybrid structures are prepared by subsequent physical vapor deposition of 6P on ZnO(1010) templates followed by overgrowth with ZnO.



Application of ultramicrotomy for HRTEM specimen preparation and imaging under different focus conditions provides direct access to the atomic and molecular structure of the hybrid interface and the organic inclusion. The hybrid stacks reveal a high structural perfection. The 6P nanocrystallites maintain a structure as in the bulk crystal. Individual 6P lattice planes can be traced up to the lateral and top interfaces with ZnO, indicating that all interfaces are defined on an atomic/molecular level. Further evaluation of the HRTEM images reveals peculiarities of 6P growth on ZnO(1010). The common 6P β -phase coexists here with the rarely reported γ -phase. The ZnO surface structure induces two mirror-symmetric in-plane preferential orientations of the 6P nanocrystallites. The ZnO surface topography, on the other hand, is critical for the structural perfection of 6P. Although conformal growth is observed, ZnO step edges induce characteristic stacking faults in 6P nanocrystallites.

INTRODUCTION

The potential of hybrid systems combining inorganic and organic semiconductors for optoelectronic applications like light-emission and light-to-electrical energy conversion has been demonstrated recently in a series of publications.¹⁻⁶ Such hybrid structures are attractive because combination of specific features of the two material classes can compensate for deficits and promote synergistic effects, promising novel properties not found in either of the individual constituents. For optoelectronic applications, layered structures are often required where the organic material is inserted between the inorganic semiconductor layers. One example is a hybrid light-emitting diode utilizing charge injection via an inorganic semiconductor p-n junction. In such a device, embedded organic nanoaggregates can serve as a color-tunable emitter. The excitation energy from the inorganic to the organic constituent is thereby transferred via a Förster-type process.^{1-4,7} The basic feasibility to grow such structures has been demonstrated recently by taking advantage of the fact that ZnO can be epitaxially grown practically at room temperature, which is compatible with organic thin film growth.^{8,9} para-Sexiphenyl (6P) nanoaggregates deposited on ZnO templates were overgrown with ZnO, and the structure of the ZnO top layer was analyzed.⁸ It was shown that, in the space between the molecular aggregates, the ZnO overlayer grows in a coherent epitaxial fashion (required for efficient charge carrier transport), whereas atop the molecular inclusions, ZnO assumes a columnar structure with preferred *c*-axis alignment independent of the orientation of the underlying ZnO template and organic crystal termination. Furthermore, partial epitaxial overgrowth of the organic inclusion was found. For the functionality of such hybrid stacks, the integrity of the organic inclusion as well as the electronic and geometric structure of the hybrid interface is crucial. Therefore, this work focuses on the resolution of the crystalline structure of the embedded 6P nanocrystallites.

6P can be considered as a model compound because the growth of this molecule has been intensively studied over the past years on a variety of substrates; for reviews, see refs 10-13. Depending on substrate and growth conditions, two distinct thin film morphologies have been found: films composed of wedding-cake-shaped nanocrystallites containing layers of nearly upright standing molecules and needle-shaped crystallites formed by aggregation of flat-lying molecules. The anisotropy of the growth velocity is responsible for the formation of these two distinct morphologies.¹⁴ At room and elevated temperatures, 6P crystallizes in two polymorphs, the so-called β - and γ -phases, differing in the angle the molecules form with the (001) crystal plane.^{15,16} These two polymorphs are also found in thin films.^{10–13,16,17} Growth of 6P on ZnO templates has been reported as well.^{17,18} On the nonpolar $ZnO(10\overline{10})$ surface used in this study, the morphology depends on the growth conditions. Keeping the substrate at room temperature during deposition, 6P aggregates in the weddingcake morphology with coexisting β - and γ -phase crystallites.

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Deposition on $ZnO(10\overline{10})$ at elevated substrate temperatures leads to the needle-shaped crystallites, where according to X-ray diffraction the contact plane is $6P(30\overline{2})$.¹⁸ Because of the interaction with the electrostatic field being present at the $ZnO(10\overline{10})$ surface, the single 6P molecules assemble parallel to the alternating rows of Zn and O, i.e., along the $ZnO[1\overline{2}10]$ direction.¹⁹ The long axis of the needle-shaped crystallites is consequently parallel to ZnO[0001].

In the following, we analyze the crystalline structure of needle-shaped 6P nanocrystallites embedded in $ZnO(10\overline{10})$ by X-ray diffraction and cross-sectional high-resolution transmission electron microscopy (HRTEM) combined with image contrast simulations. Cross-sectionalal HRTEM studies of organic thin films are rather scarce in the literature as specimen preparation of such fragile materials is challenging. Previous works employ focused ion beam (FIB) milling for sample preparation permitting the study of layer thicknesses and chemical homogeneity.²⁰⁻²⁴ Cross-sectional HRTEM images with molecular resolution were obtained for diindenoperylene; however, the large thickness of FIB lamella (>100 nm) prevented simultaneous imaging of structural details of the inorganic material, as a large fraction of the electrons is absorbed.²⁴ Here, we employ ultramicrotomy for the preparation of TEM specimens.²⁵ With this method, TEM lamellae of a thickness down to 50 nm can be prepared, preserving the structure of 6P and allowing imaging of both the organic and inorganic components. The obtained HRTEM images give in-depth information on details of the crystalline structure, lattice defects, material interdiffusion, and homogeneity of the interface, which cannot be obtained from X-ray diffraction measurements alone. We will show that all interfaces are defined on an atomic/molecular level and reveal characteristic stacking faults in 6P introduced by the ZnO surface morphology.

EXPERIMENTAL SECTION

Hybrid stacks are grown in a tandem molecular beam epitaxy (MBE) apparatus (DCA Instruments) with interconnected growth chambers for inorganic and organic materials. ZnO(1010) wafers (Crystec) were epitaxially overgrown with a thin ZnO layer to provide a pristine surface for subsequent 6P deposition. This bottom layer is grown using the standard growth protocol.²⁶ 6P (TCI) is deposited at a deposition rate of 0.1 nm/min at a substrate temperature of T = 100 °C. The nominal thickness of the organic layer is also grown at a substrate temperature of 100 °C. The sample layout is schematically depicted in Figure 1.



X-ray reflectivity (XRR) and rocking scans are performed to determine the out-of-plane crystal structure and the mosaicity of the 6P crystallites embedded in ZnO. In XRR, the intensity of the specular reflected X-ray beam is measured as a function of the out-of-plane scattering vector q_{z} , which can be calculated from the angle of incidence of the X-ray beam θ through $q_z = \frac{4\pi}{\lambda} \sin(\theta)$. The distribution of the misorientation of 6P crystallites, i.e., their mosaicity, is examined by performing rocking scans. These are carried out by fixing the angle of incidence θ and the detector angle 2θ at the respective values of the Bragg angle of a 6P crystal plane and rocking the sample along the ω axis. The mosaicity of the crystallites is then evaluated as the full width at half-maximum (FWHM) of the rocking curve. All X-ray measurements are conducted on a diffractometer at a Cu K α wavelength of $\lambda = 1.5406$ Å, originating from a rotating copper anode source with the sample kept at room temperature in a high vacuum chamber.

Specimens for HRTEM are prepared by ultramicrotomy. As a first step, the samples are cleaved into pieces of approximately 5 mm in length and 1 mm in width. Two pieces are glued face to face. Then, HRTEM lamellae are cut using a Leica Ultracut7 at room temperature. The lamella thicknesses are 50, 75, and 100 nm, enabling different TEM imaging conditions. The lamellae are finally transferred onto a holey carbon film.

HRTEM imaging is performed using a JEOL JEM2200FS operated at 200 kV. Because organic materials are weak phase objects, the HRTEM image contrast is rather low. Enhancement is realized by two means. First, the images are recorded at a defocus value of df = -1000nm, and second, the images are zero-loss filtered applying an energy width of 10 eV. Low dose imaging is applied for minimizing beaminduced damage, especially of the 6P molecules.

Image contrast simulations on the basis of appropriate structural models are performed and compared to measured HRTEM images to identify the structure of the interface and 6P inclusion. The input structures described in detail in the next section are created by CrystalMaker software. The interface models are caged in supercells and transferred to the JEMS software package.²⁷ The size of the supercell is 10.5 nm × 10.3 nm × 4.0 nm for the 6P/ZnO(1010) interface. The large size of the supercells hampers the recognition of contrast details at the atomic scale but closely corresponds to the selected magnification for HRTEM imaging of 100 kx. Utilizing JEMS, the HRTEM image contrast of the supercell is calculated for a series of specimen thicknesses and defocus values.

RESULTS AND DISCUSSION

Figure 2a shows an atomic force microscopy (AFM) image of a hybrid stack with a thin ZnO top layer (30 nm), assuring that the morphology of the embedded 6P nanocrystallites can still be mapped. Needle-shaped 6P aggregates are visible, which are aligned along the ZnO[0001] direction as expected for deposition at elevated temperatures on this surface.¹⁸ The line profile in Figure 2b gives an estimate of the height and width of the embedded nanocrystallites. The 6P out-of-plane crystalline order is uncovered by X-ray reflectivity measurements (see Figure 2c). Despite ZnO overgrowth, a Bragg reflection at $q_z = 1.64 \text{ Å}^{-1}$ corresponding to the 6P(302) lattice plane is detected, demonstrating the high structural perfection of the embedded nanocrystallites. As the distance between (302) lattice planes in the β - and γ -phases is very similar, this reflection cannot be used to distinguish the two 6P polymorphs. Furthermore, in the low q_z range, Kiessig oscillations are visible with a period corresponding to the thickness of the ZnO layer on top of 6P, indicating a conformal overgrowth.

For the mosaicity to be studied, i.e., the angular disorder among individual 6P crystallites, rocking scans on the $(30\overline{2})$ Bragg reflection are performed at two orthogonal azimuthal



Figure 2. Surface morphology and crystalline structure of a ZnO/6P/ZnO hybrid stack containing a nominally 10 nm thick 6P layer. (a) AFM image and height profile (inset) taken along the white line. (b) Measuring geometry of X-ray rocking scans and schematic depiction of the sample geometry. (c) X-ray reflectivity and rocking scans (inset) of the 6P(302) Bragg reflection along ZnO[0001] (green) and ZnO[1210] (blue).

orientations of the sample (see Figure 2b and inset of Figure 2c). The mosaicity along ZnO[0001] is considerably smaller than along the perpendicular [1210] direction. This finding can be rationalized considering the specific corrugation of the $ZnO(10\overline{10})$ surface characterized by the formation of elongated terraces along the ZnO[0001] direction. The terraces are separated by several monolayer deep trenches. 6P nano-aggregates adapting to this corrugation of ZnO therefore exhibit tilts in the [1210] direction as schematically depicted in Figure 2b, causing the larger width of the rocking curve in this direction as compared to the perpendicular direction where such tilts are absent.

Deeper insight into the crystalline order of the 6P inclusions as well as of the ZnO/6P interfaces is obtained by crosssectional HRTEM. For these experiments, the deposited amount of 6P is reduced nominally to 2.5 nm, and the ZnO top layer thickness is increased to 100 nm to provide better stability of the HRTEM lamellae. A representative selection of HRTEM images is shown in Figure 3. The light gray contrast represents the 6P inclusion. A weak shadow of the 6P inclusion occurs as the image of diffracted and not-diffracted electron beams are slightly laterally shifted. The lamellae are cut normal to ZnO[0001], i.e., the cross section perpendicular to the long a) ZnO 6P ZnOc) c) $e^{}$ $e^{}$ 20 nm $[10\overline{10}]$ $[12\overline{10}]$

Figure 3. (a–e) Representative selection of cross-sectional HRTEM images of 6P nanoaggregates embedded in a ZnO(1010) hybrid stack. The deposited amount of 6P corresponds to a nominal layer thickness of 2.5 nm. The dark lattice fringes of the 6P nanoaggregates correspond to the (100) lattice planes. The images are recorded at an underfocus of df = -1000 nm except for the inset of (c), which is obtained at a Scherzer defocus of df = -43 nm. The scale bar in the inset corresponds to a length of 2 nm.

axis of needle-shaped 6P nanocrystallites is imaged. With an underfocus value of df = -1000 nm, the internal contrast of 6P is enhanced, and lattice fringes become visible. Such a defocus value has been found to be optimal for transfer of spatial frequencies corresponding to the 6P lattice constant (see Supporting Information). The large defocus value needed to visualize weak phase objects like organic crystals is accompanied by a loss of spatial resolution. Therefore, the atomic structure of the surrounding ZnO cannot be resolved in the images. It becomes visible by setting the focus to the Scherzer defocus²⁸ of df = -43 nm (see inset of Figure 3c), showing a lateral 6P/ZnO interface. The hexagonal ZnO structure is clearly visible. Thus, combined analysis of both 6P and ZnO is possible by just changing the defocus value. A detailed HRTEM investigation of the crystalline structure of the ZnO top layer in similar hybrid stacks can be found in a previous publication.⁸ Annular bright-field scanning TEM,²⁹ an alternative method to image light atoms under in-focus conditions, has been found to provide insufficient phase contrast of our hybrid specimen. Most remarkably, the interface between the molecular inclusion and the ZnO top layer is defined on a molecular level. Lattice



Figure 4. HRTEM image contrast simulation of the $6P/ZnO(10\overline{10})$ interface. The viewing direction is along ZnO[0001]. (a) Structural model of the $6P/ZnO(10\overline{10})$ interface and (b) corresponding calculated HRTEM images for a series of thicknesses and defocus values. (c) Superposition of a contrast-adapted calculated pattern obtained for a defocus value of df = -1000 nm and a lamella thickness of t = 100 nm (framed in green) with the measured HRTEM image in Figure 3a.



Figure 5. HRTEM image contrast simulation of a 6P/ZnO(1010) interface containing a characteristic 6P stacking fault. The viewing direction is along ZnO[0001]. (a) Structural model used as basis for the simulations. A twinning plane is introduced in the 6P layer. (b) Calculated thickness/ defocus map. (c) Superposition of a contrast-adapted calculated pattern obtained for a defocus of df = -1000 nm and a lamella thickness of t = 75 nm (framed in green) with the experimental HRTEM image of Figure 3c.

planes of 6P extend to the lateral and top interfaces of the overgrown ZnO layer without visible distortion. The seemingly blurred contrast of the ZnO-on-top-of-6P interface in Figure 3a and d can be explained by height corrugation of the 6P nanocrystallites. In those lamellae, the ZnO top layer and 6P partially overlap. No traces of interdiffusion of ZnO into the organic layer are found. This is in strong contrast to previous studies where organic materials were overgrown by vapor deposition with metals $(Au)^{30}$ or by atomic layer deposition with ZnO.^{31,32} In both cases, interdiffusion of the inorganic component into the organic film was observed on a length scale of tens to a hundred nm. Closer inspection of Figure 3a and b reveals that the 6P lattice planes are inclined with respect to the surface of ZnO either to the left or to the right by an angle of approximately 70°. X-ray reflectivity measurements revealed that the vertical growth direction of 6P is along [302]. The 6P long molecular axis is thus exactly parallel to the ZnO surface. The alignment of the needle-shaped 6P nanocrystals along the ZnO[0001] implies that 6P molecules are orientated parallel to ZnO[1210]. Therefore, the observed lattice fringes should correspond to 6P(100) planes. In the β -phase, the molecules assemble in a staggered manner resulting in an angle between the (100) and $(30\overline{2})$ plane of 71.9°, as observed in Figure 3a and b. Obviously, there is no preference for molecules to grow staggered either to the right or to the left. This leads to characteristic stacking faults upon coalescence of 6P nuclei as visible in Figure 3c. On the upper terrace (right side of the step edge on the ZnO surface), 6P molecules aggregate with the (001) lattice planes inclined to the right, whereas on the lower terrace (left side of the step edge), 6P grows with the (001) lattice planes inclined to the left. At a vertical distance of approximately 3 nm from the interface to the ZnO bottom layer, the lattice planes pass a kink and assume an inclination to

the right. The aggregate on the lower terrace thus adapts the crystallographic orientation of that on the upper terrace. The vertical distance of the kink from the ZnO substrate surface corresponds to the step height of the ZnO surface. At much lower occurrence, 6P nanocrystallites with vertical (001) lattice planes are found, indicating the presence of the 6P γ -phase (see Figure 3d). The orientation of the molecules with respect to the ZnO surface is as in the β -phase nanocrystals; however, in the γ -phase, the molecules stack exactly on top of each other, resulting in an angle between the (100) and $(30\overline{2})$ plane of 90° . Similar polymorphism was found previously in 6P nanocrystallites with (001) orientation on ZnO(1010).¹⁷ Apparently, the formation of the γ -phase occurs independently of the deposition temperature and growth direction of 6P crystallites. At strongly corrugated regions of the ZnO surface, the growth of 6P is disturbed, and the inclination of the (001) lattice planes deviates from that expected for the bulk crystal phases. An example is depicted in Figure 3e. Such growth imperfections also cause the observed larger mosaicity along the $ZnO[1\overline{2}10]$ direction found in X-ray rocking scans.

To verify the interpretation, we performed image contrast simulations of the HRTEM data in Figure 3a and c (see Figures 4 and 5, respectively). As neither X-ray diffraction nor HRTEM images provide hints for the presence of a 6P surface-induced structure or a wetting layer of different orientations as reported for deposition on other substrates,^{33,34} the bulk crystal structures of both ZnO and β -phase 6P are chosen as the basis. In- and out-of-plane orientations of 6P with respect to the underlying ZnO are ZnO[0001] \perp 6P[302] and ZnO(1010) \parallel 6P(302), respectively, following the discussion above. The interface gap is set to 0.3 nm according to ref 19. Displacement of the 6P crystal in the lateral direction is chosen arbitrarily as the exact adsorption site of 6P on the ZnO surface is not

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known from experiments, and furthermore, the HRTEM image contrast is not influenced by this parameter. The resulting structural model is depicted in Figure 4a. The calculated thickness/defocus map is shown in Figure 4b. The thickness values correspond to the achievable thicknesses of ultramicrotomy-fabricated TEM lamellae. The defocus interval starts with the Scherzer defocus²⁸ where the optimum transfer of a broad range of spatial frequencies is expected (see Supporting Information) and extends to df = -1250 nm, whereby a step width of 250 nm is chosen. The simulated images clearly show that, at larger underfocus, the phase contrast in the organic layer is enhanced. Comparing the experimental image with the calculated thickness/defocus map, the best match is found for a thickness of t = 100 nm and df =-1000 nm in agreement with experimental conditions. The superposition of the corresponding calculated pattern with the experimental image is shown in Figure 4c. Close inspection reveals that the dark contrast corresponds to the molecules and the bright fringes to the gap between them. Both the contrast at the interface, including the Fresnel diffraction, and the lattice fringe alignment are well-reproduced at the correct defocus value, confirming the presented structural model.

Similarly, the 6P nanoaggregate with the stacking fault (Figure 3c) is modeled. The structural model is modified by introducing a 180° rotation of 6P layers around an axis normal to the (302) lattice planes at a distance of 3 nm from the 6P/ZnO interface (see Figure 5a). The kink formed by the stacking fault is visible in all patterns derived for different thickness/ defocus values (see Figure 5b). The best agreement with the experimental image is obtained for a thickness of t = 75 nm and df = -1000 nm, again in agreement with experimental imaging conditions (see Figure 5c), verifying the structural model.

CONCLUSIONS

By employing ultramicrotomy and HRTEM imaging under different focus conditions, the crystalline structure of such complex specimens like inorganic/organic semiconductor hybrid structures combining weak and strong phase contrast materials can be imaged. While in-focus imaging provides the structure of the inorganic component,⁸ a large underfocus assures sufficient phase contrast to visualize lattice planes of the organic inclusion even in very thin specimens required for imaging of the surrounding inorganic material. Combined HRTEM analysis and X-ray diffraction of hybrid stacks consisting of 6P nanoaggregates embedded in ZnO reveal high crystalline perfection with all interfaces defined on an atomic/molecular level. Detailed analysis of the HRTEM images reveals the impact of the $ZnO(10\overline{10})$ surface topography on the crystalline perfection of 6P. Surface corrugations cause some degree of mosaicity of 6P nanocrystallites along the $ZnO[1\overline{2}10]$ direction and lead to a characteristic stacking fault described by a kink in the 6P(001)lattice planes. Further improvement of the 6P crystalline perfection can be achieved by varying the growth protocol of the ZnO bottom layer. For example, by changing the growth temperature, the width and height of terraces can be adjusted and thus growth imperfections in 6P avoided. The results of this study show that ZnO-on-organic interfaces can be prepared with similar structural perfection as organic-on-ZnO interfaces. This opens new opportunities for the design of novel inorganic/organic hybrid structures and a considerable functionality expansion can be foreseen. New device concepts become feasible, for example, light-emitting diodes where

organic nanocrystallites are embedded in an inorganic p-n junction or devices relying on inorganic/organic multilayer stacks.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.6b00109.

Calculated contrast transfer functions of 6P(100) for four different defocus values and HRTEM of the ZnO/6P/ZnO hybrid structure (PDF)

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Notes

The authors declare no competing financial interest.

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NOTE ADDED AFTER ASAP PUBLICATION

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