Cross-sectional TEM preparation of hybrid inorganic/organic materials systems by ultramicrotomy

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Abstract. Preparation of hybrid inorganic-organic systems (HIOS) for transmission electron microscopy (TEM) in cross sectional view is the key for understanding the interfacial structure. Strikingly different materials properties like hardness, cleavability and heat sensitivity limit the number of applicable preparation strategies. Successful preparation of a HIOS system combining ZnO and para-sexiphenyl (6P) is realized by ultramicrotomy. It is shown that the alignment of the cutting plane with respect to the (0001) cleavage plane of ZnO plays a decisive role for successful preparation of extended TEM lamellae and the preservation of the HIOS structure. In particular, for (0001) oriented ZnO substrates the optimum cut direction is parallel to the HIOS interface. In cross-sectional high-resolution TEM images (100) lattice planes of 6P are observed proving the appropriate preparation strategy.

1. Introduction

Both, inorganic semiconductors and conjugated molecules are subject of intense fundamental research. The individual systems, i.e. inorganic semiconductors or conjugated organic molecules, exhibit their own optoelectronic properties permitting numerous applications in everyday life. The combination of the two materials systems promises superior performance compared to the isolated system. The interface between both components plays a key role for the final performance. Access to the structure of the interface is provided by cross-sectional transmission electron microscopy (TEM). For TEM, appropriate samples have to be prepared. It was shown that the structure of the organic component embedded in a hybrid system can be preserved by conventional preparation with final broad beam Ar ion milling assisted by liquid nitrogen cooling [1]. The application of this strategy to our system ZnO/para-sexiphenyl (6P)/ZnO resulted in a structure shown in figure 1. Although atomic force microscopy (AFM) evidences that the 6P layer has been deposited in a well-ordered structure [2] no horizontally aligned (100) lattice planes of 6P are visible in the high-resolution TEM (HRTEM) image. The 6P region shows typical contrast of an amorphous material. Obviously, the crystalline structure of 6P was destroyed, presumably by energy transfer from the impinging Ar ions to the molecules. Hence, an alternative preparation strategy has to be identified excluding ion milling. Strategies utilizing chemical or electrochemical etching are excluded too since these methods presume chemical similarity of the individual layers which is not fulfilled for HIOS. For the preparation of soft matter, ultramicrotomy (UM) is a well-established method. Applications of UM to the preparation of hard matter were reported too [3], whereas preparation of combined hard and soft matter as functional material is still lacking. In this paper, the UM preparation of HIOS for cross-sectional TEM

investigations is described. The results are discussed with special focus on both, the crystallographic orientation of the ZnO substrate and the alignment of the UM cutting plane relative to the cleavage plane of the substrate.

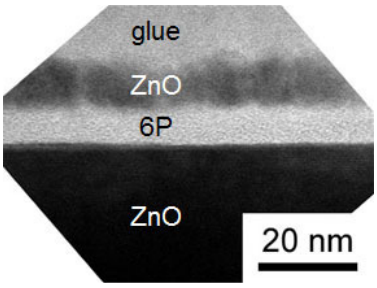

Figure 1. HRTEM image of the HIOS structure ZnO/6P/ZnO. Last step of TEM preparation was Ar ion milling combined with cooling by liquid nitrogen.

2. Samples and instrumentation

The HIOS structures were grown in a tandem molecular beam epitaxy (DCA450) equipped with separate growth chambers for 6P and ZnO. ZnO buffer layer and top layer are grown employing the standard and low-temperature epitaxial regime, respectively, described in detail elsewhere [4]. 6P growth is performed in the second chamber equipped with Knudsen type effusion cells. For growing the ZnO top layer, the substrate is kept at 100°C in order to maintain the structure of 6P. To control the growth direction of ZnO as well as the 6P film morphology, the hybrid stacks are fabricated on either $(01\bar{1}0)$ or (0001) oriented ZnO substrates. The set of samples grown for systematic studies of UM preparation is given in figure 2. The magnified insets give the projected atomic structure.

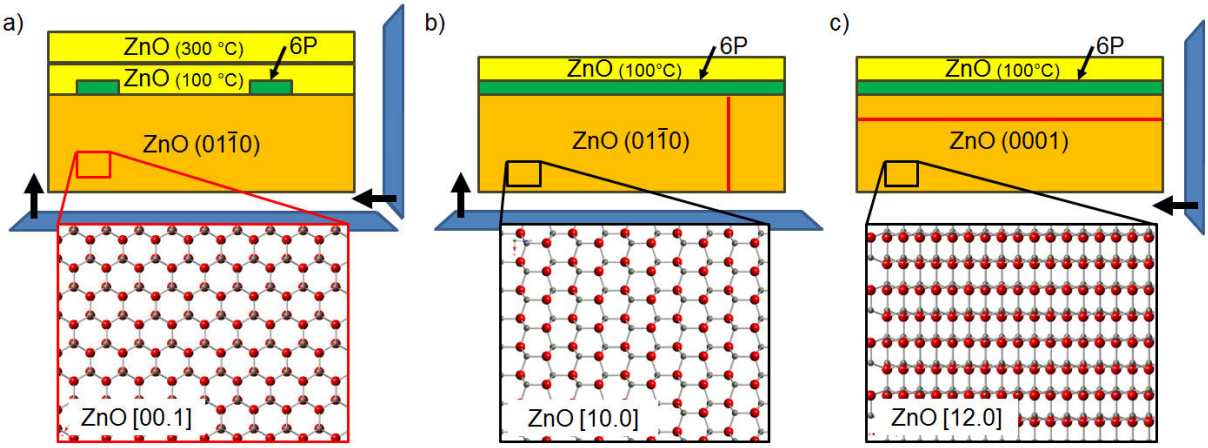

Figure 2. HIOS samples prepared by UM (a-c). The enlarged structural motives shown at the bottom represent the atomic arrangements with respect to the cutting direction (bold arrows) of the UM knife sketched in blue. In addition, the cleavage plane of ZnO is given in red.

For preparation of the samples for TEM a LEICA UltraCut7 room temperature ultramicrotome was utilized. The angle of the UM diamond knife was 35° and the cutting speed was set to 0.1 mm/s. Lamellae were transferred utilizing a magic loop tool from the water trough of the UM knife onto holey carbon film hydrophilized by glow discharge.

TEM imaging was performed in a JEOL JEM2200FS equipped with in-column energy filter. For enhancing the contribution of the organic component to the image contrast, a 10 eV energy slit was inserted selecting the zero-loss electrons and blocking those suffering electron losses of the carbon plasmon at about 25 eV. High-resolution TEM imaging was performed at an underfocus of 1000 nm.

3. Results and discussion

In order to systematically study the success of UM preparation, several alignments of the UM cutting plane, cutting direction, and cleavage plane of the ZnO substrate were investigated. In all cases face-to-face glued samples were used ensuring symmetric geometry of the sample for the cutting process.

In figure 3, the results of UM cutting *parallel* to the (0001) cleavage plane of ZnO are given (cf. figure 2a). When UM cut is performed *along* the inorganic/organic interface the HIOS is preserved only incompletely (cf. figure 3a). In particular, the ZnO columns grown atop 6P were partly removed

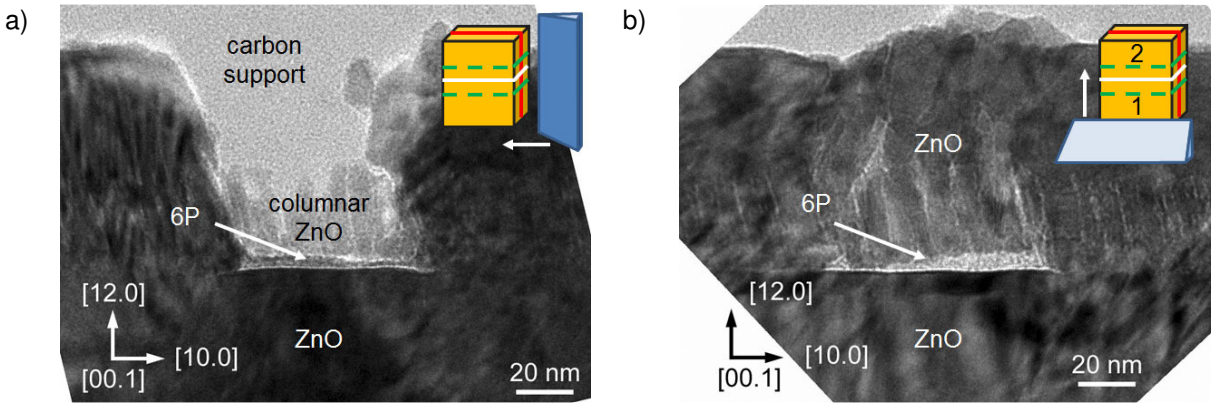

Figure 3. HIOS after UM preparation with cutting plane *parallel* to cleavage plane marked by red line. The direction of UM cut (see white arrows) was aligned a) *along* and b) *normal* to the HIOS interface.

due to shear forces acting normal to the column axis. Consequently, the apparent specimen thickness in this region is reduced. Moreover, the upper part of the ZnO layer grown atop 6P is completely missing. The inset of figure 3a shows schematically the face-to-face glued specimen and both the position of the UM knife and the cutting direction. The cleavage plane is marked in red.

In contrast to the alignment chosen for figure 3a, the HIOS is fully preserved when the cutting direction is aligned normal to the HIOS interface (figure 3b). There are two different scenarios for a face-to-face glued sample. When the UM cut progresses from the ZnO substrate towards the HIOS side of the sample the HIOS components are stretched and initial structure is not preserved (cf. area 1). On the opposite side of the sample (area 2), i.e. after crossing the glue line (see the white line in the inset of figure 3b), the HIOS components are kept attached to each other. As a result of the forces acting during UM cut, the lamellae are separated at the glue line into the initial sample parts. Moreover, the lamellae are fragmented into needles with their axis aligned parallel to the edge of the UM knife. Concerning preservation of the 6P structure one would expect to see (100) lattice planes aligned parallel to the [12.0] direction of ZnO. However, no indication for this is found. This can be attributed to the particular MBE growth procedure (cf. figure 2a). The growth temperature of 300 °C applied during the second step of ZnO overgrowth exceeded the critical temperature for amorphization of 6P.

Figure 4 shows results of a second UM preparation applied to the samples sketched in figure 2b) and c). In both cases the cleavage plane of ZnO was aligned *normal* to the UM cutting plane. It has to be pointed out that for both set-ups complete lamellae were gained and no fragmentation appeared. Figure 4a represents the result for UM cutting *normal* to the HIOS interface. Due to the nominal 6P layer thickness of 1 monolayer a visibility of (100) lattice planes cannot be expected. Nevertheless, the

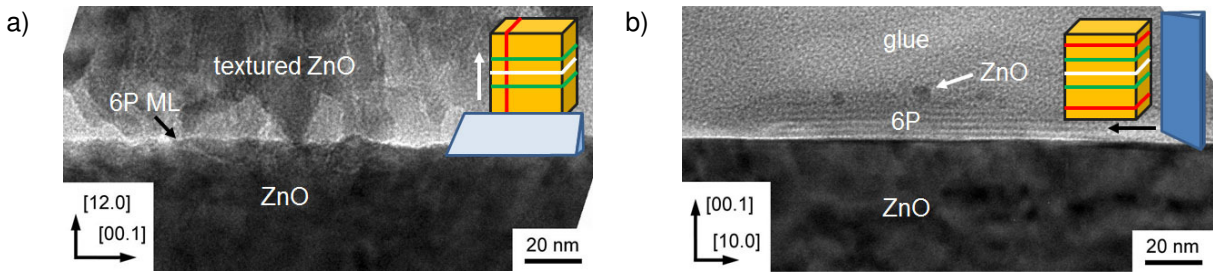

Figure 4. HIOS after UM preparation with cutting plane *normal* to cleavage plane (marked by red lines). The cutting direction was aligned *in-plane* to the cleavage plane (see white arrow in a) and black arrow in b)). Owing to the different substrate orientation the direction of UM cut was aligned a) *normal to* and b) *along* the HIOS interface.

correlation between ZnO substrate and the ZnO top layer was maintained. The presence of 6P is indicated by both, the ZnO top layer exhibiting textured structure as revealed by electron diffraction and the higher intensity at the HIOS interface in the TEM image due to weak interaction between organic material and transmitted electrons.

Full preservation of the crystalline structure of 6P is evident from figure 4b. Here, the UM cut was performed parallel to the HIOS interface. A 6P island of a height of about 20 nm is visible in contact with the (0001) oriented ZnO substrate. Lattice planes are clearly recognized within the 6P.

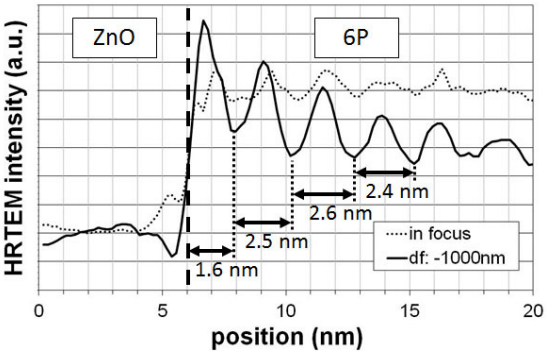

Figure 5. HRTEM image intensity profiles across the HIOS interface (dashed line) taken from figure 4b (solid) and from an image acquired at in-focus conditions (dotted).

In order to understand the arrangement of 6P molecules at the HIOS interface an intensity profile is taken from figure 4b (see solid line in figure 5). The distance measured for the second, third, and fourth lattice plane amounts to about 2.5 ± 0.1 nm, which corresponds to the (100) lattice planes of 6P. The interpretation of the first lattice plane having a thickness of 1.6 nm is not straightforward. This becomes obvious when a second profile taken from an in-focus image of the same region is compared (see dotted line in figure 5). On the one hand the increase of contrast for large defocus is nicely reproduced. But on the other hand, a shift of the position of the lattice planes is observed. Since the HRTEM imaging process is strongly affected by defocussing, any direct interpretation of the interfacial structure becomes impossible. In order to assess the real interface structure, exit wave reconstruction has to be performed based on defocus series. The exit wave of the object can be obtained by back propagation of the image wave taking into account the contrast transfer function for the applied HRTEM imaging conditions.

Looking back to figure 4b, atop 6P nano-crystallites of the non-continuous ZnO cap layer are seen. The amorphous glue is still in contact with the layers indicating both, appropriate UM cutting procedure and preservation of the initial arrangement of the HIOS components.

4. Conclusions

UM is an appropriate method to prepare cross-sections of HIOS for TEM investigation. In comparison to ion milling based methods, UM is realized without thermal treatment, thus any modification of the organic component upon heating is ruled out. In order to achieve optimum TEM samples the alignment of both, UM cutting plane and cutting direction with respect to the cleavage plane of the substrate have to be considered. As long as the cutting direction is aligned in-plane to the cleavage plane of the ZnO substrate extended lamellae are gained. For samples with the HIOS interface oriented parallel to the (0001) plane of ZnO both, the structure of 6P and the contact to the substrate were preserved. 6P is deposited as a crystalline layer onto (0001) ZnO substrate with the (100) lattice planes parallel to the ZnO surface.

Acknowledgement

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