Soft Matter, Polymers, Composites

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HRTEM imaging of inorganic/organic interfaces

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The interfacial structure of hybrid inorganic/organic systems (HIOS) strongly influences their resulting physical properties. The inorganic component comprises, e.g., semiconducting materials for optoelectronic applications. In our case an extended single crystalline (0001) oriented ZnO substrate was selected. On the organic side there are conjugated molecules exhibiting a delocalised π system making the electrons available for charge transport. Para-sexiphenyl (6P) was selected for our HIOS model system. The arrangement of the molecules on the semiconductor surface is subject of vivid fundamental research. From atomic force microscopy performed after deposition of the 6P layer some information is gained on its morphology including lateral size and height of islands formed at the semiconductor surface [1]. But the evolvement of the deposition of multilayer 6P cannot be recognized by a top-view analysis after growth. Here either in-situ measurements by gracing incidence X-ray scattering [2] or – and this is the focus of this work – cross-sectional transmission electron microscopy (TEM) imaging can give valuable information. For gaining electron transparent cross-sectional specimen special care has to be taken with respect to the striking different materials properties of both components of HIOS. An appropriate route for cross sectional TEM preparation by room temperature ultramicrotomy was described elsewhere [3]. This route was applied here and resulted in a TEM specimen thickness of about 100 nm. TEM investigations were performed utilizing a TEM/STEM JEOL JEM2200FS operated at 200 kV. The 2200FS is equipped with an in-column energy filter utilized here for increasing the image contrast by inserting a slit of a width of 10 eV. Thus only elastically scattered electrons contribute to imaging.

Figure 1 shows two high-resolution TEM (HRTEM) images of the same HIOS interface area recorded for Scherzer focus (a) and for a defocus of about -1000 nm (b). The dark spots atop 6P of about 10 nm in diameter originate from ZnO nanoparticles deposited after 6P growth. The large defocus was chosen in order to enhance the phase contrast of 6P. The effect is clearly seen comparing the line scans extracted across the interface between ZnO substrate and 6P (see Fig. 1c). The dotted line corresponds to Scherzer defocus and the solid line corresponds to a defocus of -1000 nm. In order to analyze the periodicity of the 6P lattice planes the position of the HRTEM intensity maxima were identified and the inter-planar distances were extracted. The distances given in Fig. 1c are taken from the profile of the image defocused by -1000 nm. The position of the first lattice plane can hardly be seen since the fringe contrast due to Fresnel diffraction at the interface is superimposed. But comparing the two profiles, a first 6P lattice plane can be recognized at a distance of about 1.0 nm from the HIOS interface. The inter-planar distance increases to 2.4 nm within the next two monolayers.

In order to optimize the defocus condition for identifying all the 6P lattice planes several defocus series were acquired with non-linear focus change ranging between 0 nm and -2000 nm (cf. Fig. 2). 6P lattice plane positions were identified for the full set of images by an own software routine from intensity line scans taken across the HIOS interface and laterally averaged within the area marked in Fig. 2a. The results are given in Fig. 2b (see open symbols). For the entire focus series the position of the individual lattice plane remains almost constant. Against that, the position d of the Fresnel fringe changes with defocus Δf. In a first approximation this behavior can be described by $d = \sqrt{(\Delta f * \lambda)}$; λ-wavelength (see solid line in Fig. 2b). Consequently, for a certain focus range the fringe superimposes to the first 6P lattice plane hampering their identification. But with increasing defocus the fringe shifts and the first 6P lattice plane can be located as shown in Fig. 1c. The defocus scale was adjusted to zero focus by extrapolating the function of Fresnel fringe position to zero value.

The data extracted from defocus series of HRTEM images prove that the alignment of 6P molecules undergoes a modification from almost lying parallel to the ZnO surface to standing almost upright which corresponds to the monoclinic bulk structure of 6P. Thus from HRTEM measurements valuable information is gained for understanding the structure of the HIOS interface.

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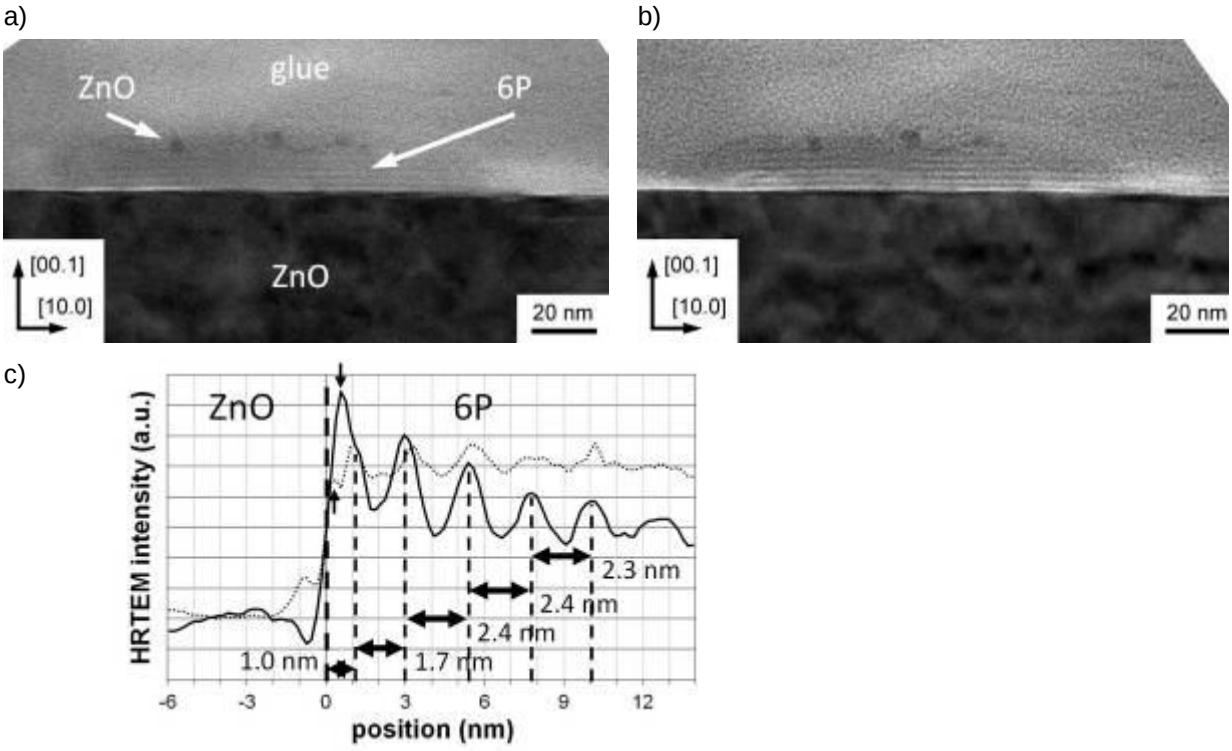

Figure 1. HIOS interface analysis by HRTEM imaging using only elastically scattered electrons: a) Scherzer defocus image showing weak phase contrast, b) enhanced phase contrast at a defocus of -1000 nm, c) HRTEM intensity profiles taken from scans across the HIOS interface (bold dashed line). Dotted line: Scherzer defocus image, solid line: out-of-focus image. The distances between the identified lattice planes are measured between maximum positions of the HRTEM intensity. The first maximum of both profiles (marked by vertical arrow) is due to diffraction at the interface. It shifts with defocus

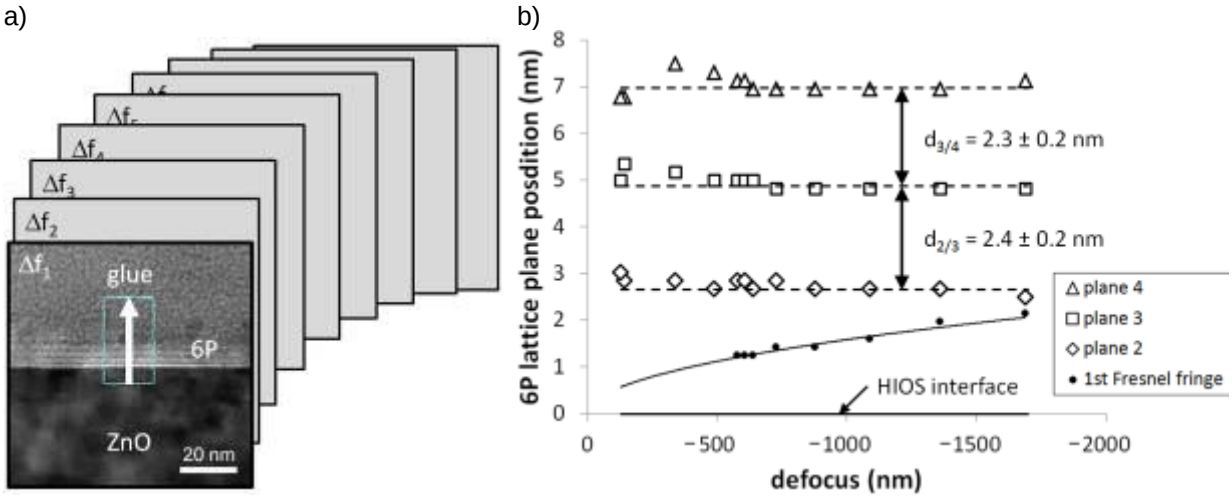

Figure 2. Distance of lattice planes from the HIOS interface for a series of defocused images: a) sketch of defocus series with indicated line scan position, b) distance of 6P lattice planes from the HIOS interface depending on defocus. The dots correspond to the detected position of the 1st Fresnel fringe due to diffraction at the HIOS interface. The solid line corresponds to the calculated position if the first Fresnel fringe.