Functional Materials

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Three dimensional characterization of nanofilamentous growth of transition metal oxide dopants in organic semiconductors

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Organic semiconductor devices are typically limited by low intrinsic conductivity and high charge injection barriers at the contacts which can be overcome by electrochemical doping. Wide bandgap materials like 4,4′-Bis(N-carbazolyl)-1,1′-biphenyl (CBP), which are commonly used in organic light emitting diodes, can be p-type doped with transition metal oxides like MoO_3 in a co-evaporation process. Often high doping ratios, exceeding 10 vol%, need to be applied due to low doping efficiencies of 1-2% [1]. Here we investigate the morphology of CBO:MoO_3-composites with films of varying dopant/matrix ratios. Bright-field transmission electron microscopy (TEM) and electron spectroscopic imaging (ESI) [2] of CBP films doped with 10 and 33 vol% MoO_3 revealed that at room temperature MoO_3 forms agglomerations. For 10 vol% doping concentration these agglomerations are about 1nm in diameter and typically spaced about 7 nm apart. A much larger doping concentration of 33 vol% leads to an increased densitiy of MoO_3 agglomerates of similar diameter as before. Electron-tomography revealed that for 10 vol% doping concentration MoO_3 forms filament-like agglomerates preferentially oriented along the growth direction of the film [3], as seen in Fig. 1. A large part of the filaments extends throughout the film thickness. The presence of these large clusters can explain the low doping efficiency discussed above. The 3D reconstruction of a sample with greatly reduced dopant concentration (0.6 vol%) in Fig. 2 shows that MoO_3 filaments – again with similar diameter – still form during co-evaporation. However, a significant decrease in filament number as well as possible fragmentation of the filaments is observed. Electrical measurements parallel and orthogonal to the growth direction of the filaments indicate an anisotropic charge transport for 10 vol% MoO_3 doping concentration. In contrast, measurements of the sample with 0.6 vol% dopant concentration show an isotropic behavior. These conductivity measurements can consistently be explained with the morphologies observed from electron tomography. Continuous filamentous transition metal oxide clusters can lead to an increased conductivity in the direction of the filaments (Fig. 1) whereas for lower dopant concentration the discontinuous clusters do not contribute to a preferred direction of conductivity.

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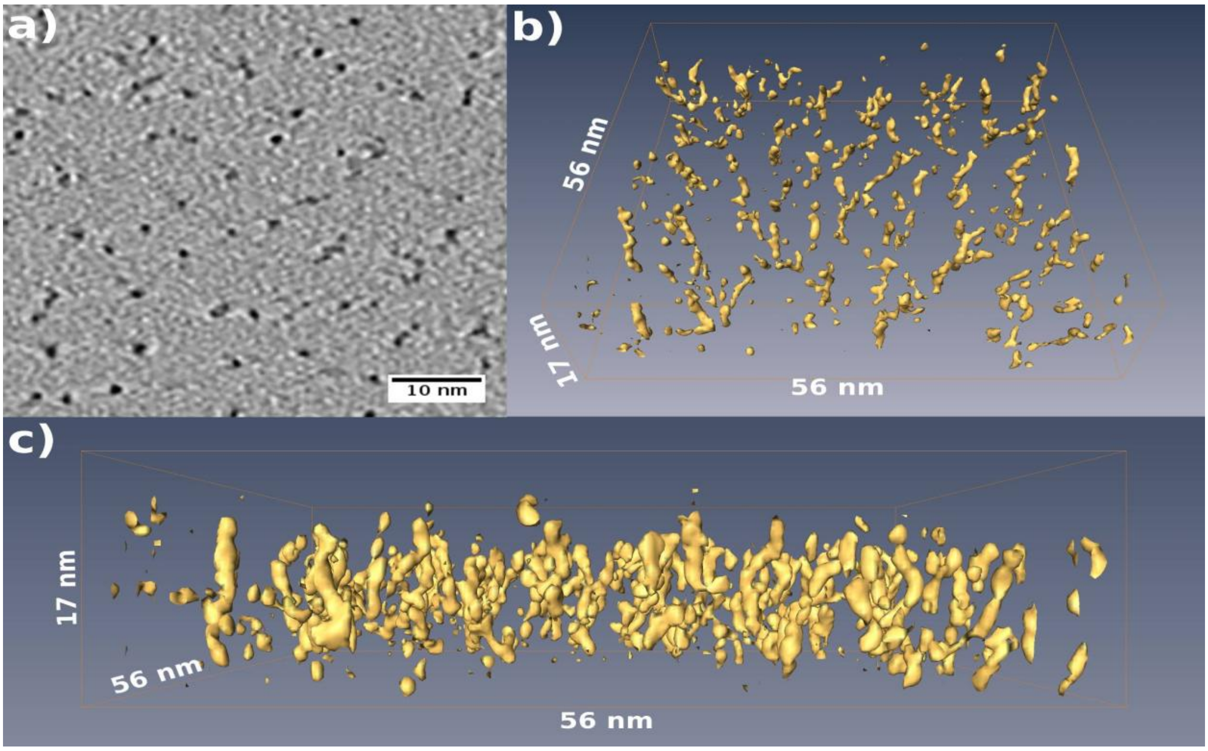

Figure 1. a) Grey-scale image of xy-plane of 10 vol% MoO_3:CBP. Three dimensional representation of the MoO_3 filaments, b) segmentation in 3D and c) side-view of yz-plane.

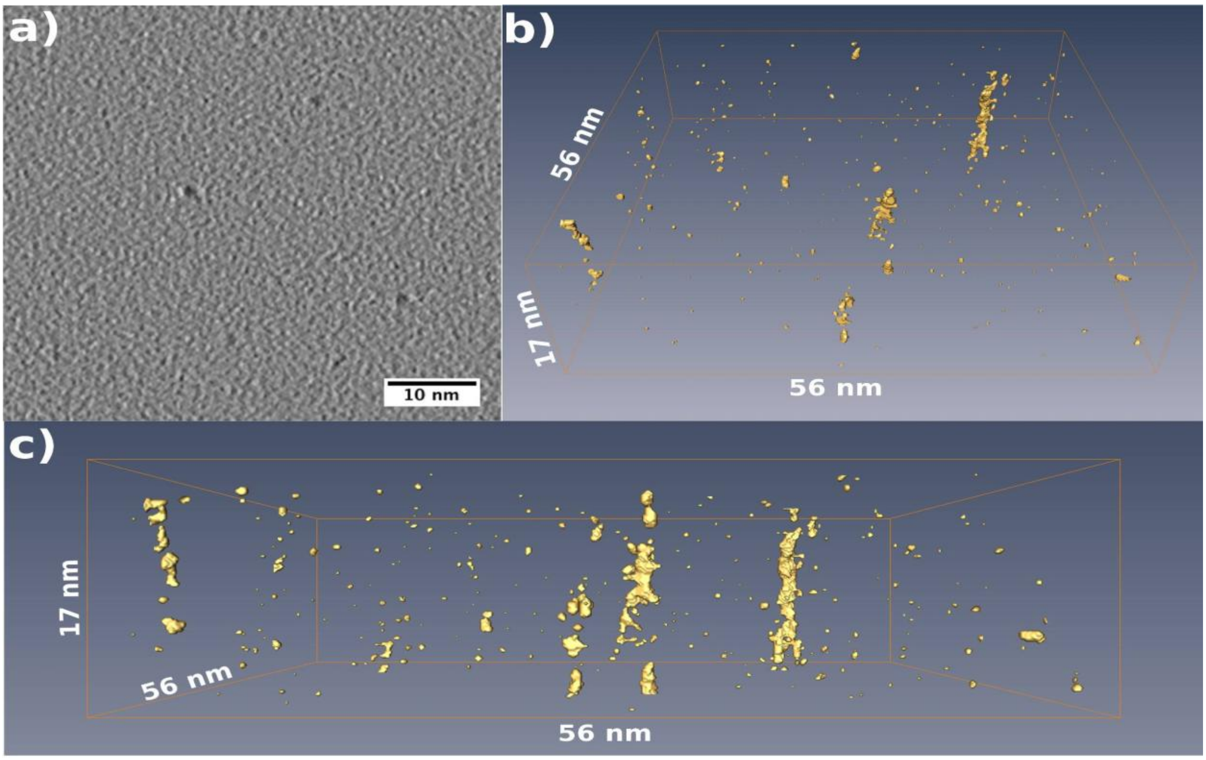

Figure 2. a) Grey-scale image of xy-plane of 0.6 vol% MoO_3:CBP. Three dimensional representation of the MoO_3 filaments, b) segmentation in 3D and c) side-view of yz-plane