Supporting Information

Nanowire-Array Films of Copper Hexadecafluorophthalocyanine (F_{16}CuPc) Fabricated by Templated Growth

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Growth of F_{16}CuPc on a PTCDA template layer deposited on indium tin oxide (ITO)

Figure 1 shows the morphology of the PTCDA template layer and the F_{16}CuPc pristine and templated films grown on an ITO/glass substrate. The template layer is composed of spherical crystals (Fig. 1a), similar to that seen after deposition on SiO₂ substrate. The F_{16}CuPc thin films grown on bare ITO have a morphology characterised by spherical-like or needle-like crystals (Fig. 1b). When the F_{16}CuPc films are grown on PTCDA/ITO, the FE-SEM images show that the templated F_{16}CuPc films are no longer composed of needle-like crystals, but instead are characterised by standing-up nanowire-array crystals (Fig. 1c). The F_{16}CuPc crystals are very flexible which can be seen during electron beam exposure in the FE-SEM experiments. Exposure to an electron beam of low acceleration voltage leads to bending of the surface nanowire crystals, which become more entangled and results in formation of a dense standing-up network. Cross-sectional FE-SEM images show the formation of the nanowire-array crystal films on the PTCDA template (Figs. 1d and 1e). Different thicknesses of the initial PTCDA template layer (5 nm and 70 nm in Figs. 1d and 1e respectively) have the same effect on the growth of the F_{16}CuPc films.
**Figure 1** Morphology of the PTCDA template layer and the F$_{16}$CuPc pristine and templated films grown on ITO: (a) PTCDA (5 nm), (b) F$_{16}$CuPc (35 nm), (c) F$_{16}$CuPc (75 nm)/PTCDA (5 nm), (d) cross-sectional image of F$_{16}$CuPc (75 nm)/PTCDA (5 nm), (e) cross-sectional image of F$_{16}$CuPc (75 nm)/PTCDA (70 nm).

XRD results of the PTCDA template layer and the F$_{16}$CuPc pristine and templated films grown on ITO are shown in Fig. 2. The (002) diffraction peak only appears in the pristine F$_{16}$CuPc films, while the peak disappears and a new peak at 28.4° (d = 3.14 Å) emerges when grown on the PTCDA template, indexed as a (122) diffraction peak. The presence of this new peak clearly indicates the change in molecular orientation after growth on the PTCDA template layer. According to the corresponding single crystal data (a = 4.7960 Å, b = 10.228 Å, c = 28.002 Å, α = 86.41°, β = 87.89°, γ = 81.39°), the (002) diffraction peak suggests that the F$_{16}$CuPc molecules are aligned in a standing-up arrangement, while the (122) peak corresponds to a lying-down arrangement.
Figure 2 XRD $2\theta$ scans of the PTCDA template layer and the $F_{16}$CuPc pristine and templated films grown on ITO. The curves correspond to (a) 75 nm $F_{16}$CuPc, (b) 75 nm $F_{16}$CuPc/5 nm PTCDA, (c) 75 nm $F_{16}$CuPc/20 nm PTCDA, (d) 75 nm $F_{16}$CuPc/70 nm PTCDA and (e) 70 nm PTCDA. The ITO diffraction peak of the (222) crystal plane is provided as a reference. The diffraction peak at $2\theta = 6^\circ$ in the pristine film disappears in the templated films, while a new peak at $28.4^\circ$ emerges. This suggests that the $F_{16}$CuPc molecules arrange with a lying-down configuration in the templated films instead of the standing-up configuration in the pristine films.

References