Supporting Information

Nanowire-Array Films of Copper Hexadecafluorophthalocyanine (F₁₆CuPc) Fabricated by Templated Growth

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Growth of F₁₆CuPc 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 grow 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 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°),¹ 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 θ 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° 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

(1) Yoon, S. M.; Song, H. H.; Hwang, I.-C.; Kim, K. S.; Choi, H. C. *Chem. Commun.* 2010, 46, 231-233.