Fabrication of oriented conductive metal-organic framework thin film by dry process

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Metal–organic frameworks (MOFs) consist of metal ions and ligands that show crystalline porous structure. Recently, electrically conductive two-dimensional (2D) MOF, $Cu_3(HHTP)_2$ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), attracts attention in device applications such as electronics and chemiresistive sensors [1,2]. For such applications, the oriented thin film is desired due to its anisotropic property and structure, and has been fabricated by the wet process [3]. Compared to the wet process, the dry process shows the advantage of device fabrication because of reduced damage at the interface caused by solvent. However, no report is available for the synthesis of orientated $Cu_3(HHTP)_2$ thin film by dry process. In this study, we show a novel two-step dry process combining vapor phase deposition and pyridine vapor annealing to fabricate oriented $Cu_3(HHTP)_2$ thin film.

As a first step, $Cu_3(HHTP)_2$ thin films were deposited on Al_2O_3 (0001) using infrared-pulsed-laser deposition (IR-PLD) [4,5]. $Cu(OAc)_2$ (copper acetate anhydrous) and HHTP were mixed with infrared absorbers (Si), followed by pelletization to make metal and ligand targets, respectively. The thin films were deposited at 100 °C in a multilayer form: alternate deposition of HHTP layer (10 nm) and $Cu(OAc)_2$ (8 nm) was repeated 5 times. As a second step, the fabricated multilayer films were annealed under pyridine vapor; the deposited film and a 3 μL of pyridine were separately set in a gasket-sealed cell (7 ml) under air. The cell was annealed at 60 °C for 24h. The structural characterization was performed by X-ray diffraction (XRD).

XRD patterns indicate the formation of oriented $Cu_3(HHTP)_2$ thin film (Figure). The out-of-plane pattern only shows a broad peak near 28°, originating from the interlayer spacing of $Cu_3(HHTP)_2$ 002 (red star). In the in-plane pattern, sharp peaks corresponding to the 100, 200, and 210 Miller indices were observed. Thus, in-plane orientation may be at random, confirming the successful fabrication of (001)-oriented $Cu_3(HHTP)_2$ film.

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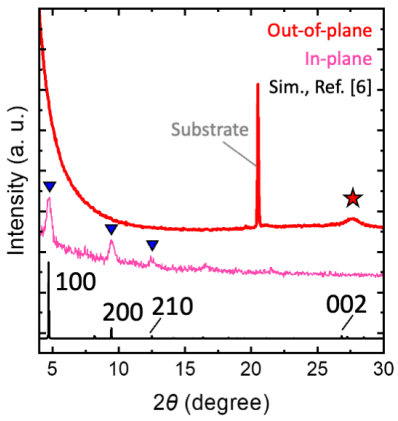

Figure : X-ray diffraction patterns of the film.