Experimental report

06/04/2020

Proposal: 1-04-162 **Council:** 10/2018

Title: Following tellurium deposition in mesoporous cubic silica by in situ time-of-flight GISANS

Research area: Chemistry

This proposal is a new proposal

Main proposer: Gilles Ernest MOEHL

Experimental team: LI SHAO
Gilles Ernest MOEHL

Local contacts: Robert CUBITT

Samples: Mesoporous cubic silica film

Instrument	Requested days	Allocated days	From	To
D33	4	4	19/09/2019	23/09/2019

Abstract:

Mesoporous silica films with 8-10 nm pores have been produced in our labs by Evaporation Induced Self Assembly (EISA). These shall be used as template for the fabrication of nanostructured thermoelectric devices, which requires the electrodeposition of Te into the porous structure. Diffusion into the pores is limited due to their size, which is why ultra-short pulses have to be used in order to obtain homogeneous filling as otherwise, individual pores might fill up quickly and become the center of deposition. Using TOF-GISANS, we want to reveal under which conditions the deposition happens from the bottom to the top of the film and at which depth the likelihood of parasitic nucleation is highest. This experiment will also indicate, whether the filling of the cubic network with a hexagonal structure is possible, which might happen in the mass-transport limited deposition regime.

Following tellurium deposition in mesoporous cubic silica by in situ time-of-flight GISANS

Experimental team: GILLES MOEHL, LI SHAO, ROBERT CUBITT

The process of bismuth electrodeposited into the porous of mesoporous silica film was investigated by in-situ grazing-incidence small-angle neutron scattering (GISANS) technology in 09.2019 in ILL.

Template preparation

Three-dimensional highly ordered mesoporous silica films with 8-10 nm pores were prepared on 65mm*30mm Pt-Silicon substrates in our labs by evaporation induced self-assembly (EISA) method. Fig 1(1) shows the GISAXS pattern of the prepared film, which corresponds to Fmmm structure.

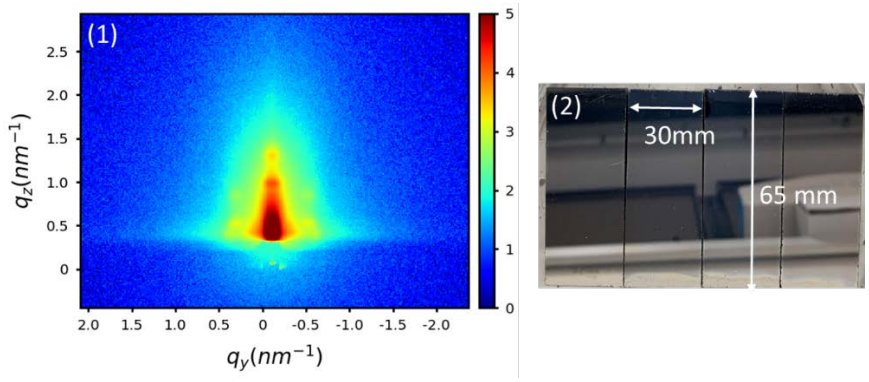

Fig 1(1) The GISAXS pattern of the mesoporous silica film using as templates; (2) The mesoporous silica film coted on Pt substrates.

Template electrodeposition

By using these films as templates, Bi nanowires were electrodeposited into the three-dimensional porous structure. The small nanoporous template are a big challenge for electrodeposition. Hence, it is of significance to explore the electrodeposition process. A sealed cell was designed to conduct the electrodeposition experiment, as shown in Fig 2. A cyclic voltammogram obtained from the 5mM $[N^nBu_4][BiCl_4]$ in dichloromethane containing 0.1 mol/L $[N^nBu_4]Cl$ as the supporting electrolyte. The voltammetry starts with a steep deposition at -0.28V, followed by a reduction peek at -0.51 V, which suggests the Bi^{3+} is reduced to Bi. In anodic scan, there is a diffusion-limited deposition area. The stripping peak is in 0.46 V. Two step pulse electrodepositon (PED) with different conditions were used to deposit Bi nanowires into the mesoporous. First, a lower potential was used to create more nuclei, which is called nucleation process. The following higher potential (growth process) allowed the nuclei grow gentle and uniformly. Seven samples were prepared during the three days beam time. The detailed conditions of each sample were listed in Table 1.

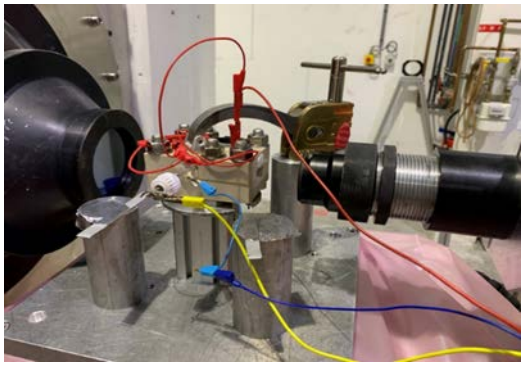

Fig 2 The experiment setup. The middle part is the designed cell connected to the potentiostat.

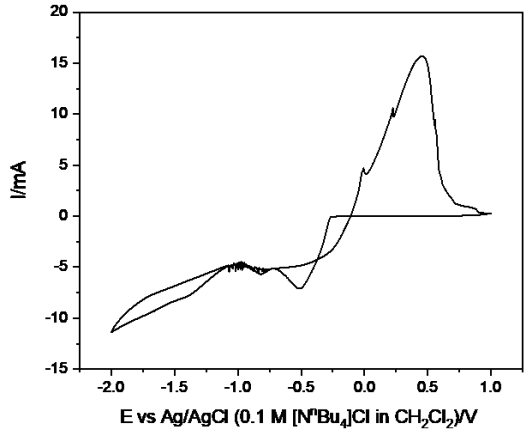

Fig 3 Cyclic voltammogram

Table 1 The PED conditions of the prepared samples.

	Nucleation process	**Growth process**
Sample 1	-1.5V, 1.2s, once	-0.25V, 1.2s, 600 times
Sample 2	-2.0 V, 1.2s, once	-0.25V, 1.2s, 600 times
Sample 3 (Grafted)	-1.5V, 1.2s, once	-0.25V, 1.2s, 600 times
Sample 4	-1.5V, 1.2s, once	-0.5V, 1.2s, 20 times
Sample 5 (Grafted)	-1.5V, 1.2s, once	-0.5V, 1.2s, 20 times
Sample 6 (BiTe)	-2V, 1.2s, once	-0.5 V,1.2s once
Sample 7	-2V, 1.2s, once	-0.5V, 1.2s, 20 times

In-situ grazing-incidence small-angle neutron scattering

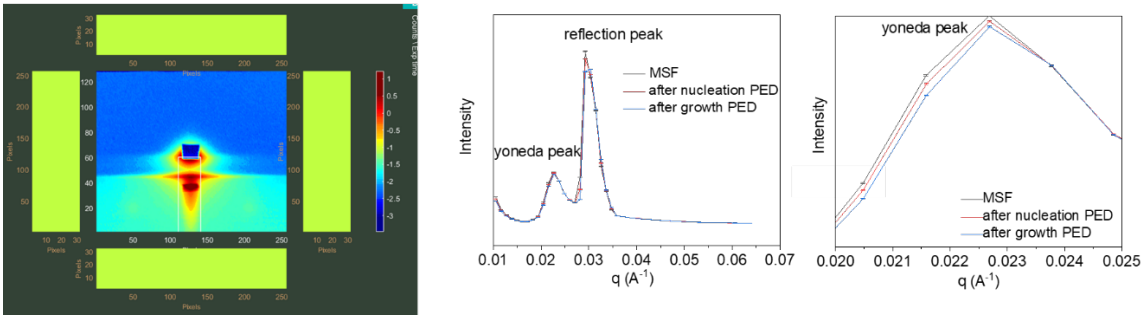

Fig 4 The GISANS pattern of sample 7 and the Qz cut.

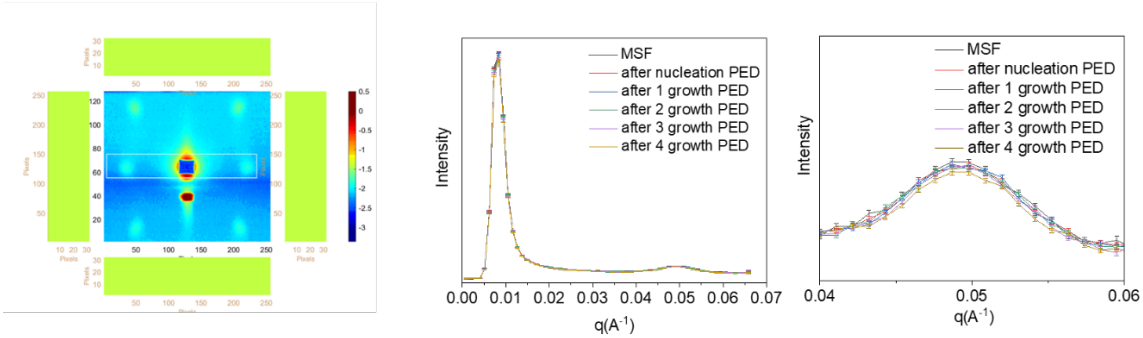

Fig 5 The GISANS pattern of sample 5 and the Qy cut.

Sample 1 and sample 2 experiences long time deposition. During the PED, we collected the neutron patterns in each pulse. The short collection time leads to tiny change in GISANS. For sample 5 and sample 7, we obtained a series GISANS patterns by decreasing the pulse times and increasing the GISANS collection time. As shown in Fig 4 and Fig 5, the vertical and horizontal integration of sample 7 and sample 5 shows the intensity of Bragg peaks decreased with the increase of deposition time. In theory, the scattering length density of Bi is higher than solvent DCM, resulting in the contrast between Bi and silica template is lower than DCM and silica template. Thus, the intensity of Bragg peaks will decrease after the PED, which correspond to the results of the experiments.

However, not all the intensity of peaks decrease. Some peaks didn't change or even increase a little. More analysis work will do in the following months. Sample 3, 4 and 6 failed because of the connection problems during the experiment.