# Experimental report

09/04/2019

**Proposal:** **1-04-145** **Council:** 4/2018

**Title:** In situ GISANS study on the electrodeposition of bismuth telluride ontitanium nitride from non-aqueous solution.

**Research area:** Chemistry

**This proposal is a new proposal**

**Main proposer:** **Gilles Ernest MOEHL**

**Experimental team:** Samuel FITCH
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**Local contacts:** Robert CUBITT

**Samples:** TiN on Si wafer

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D33 | 3 | 3 | 12/10/2018 | 17/10/2018 |

## Abstract:

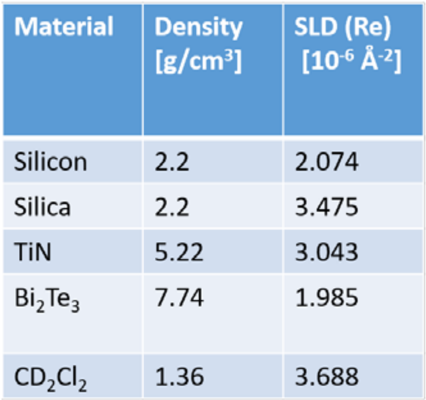
Bismuth telluride films on titanium nitride substrates have been electrodeposited in our lab from a non-aqueous electrolyte based on dichloromethane. The particle density on the substrate surface, their shape and size distribution depends on the applied deposition potential and time. In principle, it should be possible to deposit the material with a high density of nuclei at the beginning, followed by a uniform particle growth. The proposed GISANS experiment aims at investigating the nucleation process of bismuth telluride on titanium nitride during electrodeposition, by exploiting the evanescent wave of neutrons in total reflection through the back of the sample, which allows for the monitoring of nucleation and growth inside a closed electrochemical cell by precisely tuning the neutron penetration depth.

# In situ GISANS study on the electrodeposition of bismuth telluride on titanium nitride from non-aqueous solution.

Experimental Team: MOEHL Gilles, FITCH Samuel, HECTOR Andrew, CUBITT Robert

Under the Advanced Devices by Electroplating EPSRC programme grant (EP/N035437/1, July 2016) we are working on the integration of high quality chalcogenide semiconductors with microfabricated structures to be used in devices as thermoelectrics, phase change memory (PCM) and infra-red detectors. The full potential of these devices has not been deployed so far due to the non-availability of the required functional materials, fulfilling the required demands regarding quality and controlled deposition techniques. Using weakly-coordinating solvents like dichloromethane (DCM), the successful deposition of a material into a nanoporous template is defined by a homogeneous deposition with a filling efficiency approaching unity. In order to achieve this, the deposition process has to be highly controlled, where nucleation occurs in all pores simultaneously. Therefore, one major element of interest to this project in general is understanding the earliest step of deposition: nucleation. The investigation of nucleation at the nanoscale represents a major issue for many microscopy techniques, where samples can only be analysed post mortem as the process happens in the liquid phase, especially when studying patterned substrates where individual layers have to be cross sectioned. Time resolved measurements on a system that represents the actual targeted manufacturing process may only be done by using scattering techniques. By doing so, the formation of particles, their shape, arrangement and growth can be followed inside an actual electrochemical cell. Grazing incidence X-ray scattering (GISAXS) has been used in the past to follow a variety of deposition processes in situ, including sputtering, spray deposition and electrodeposition[1–5]. The latter technique presents the issue of a so called "buried interface"[6], which means that for grazing incidence techniques a favourably large footprint on the sample leads to an enlarged attenuation of the beam due to the pathway through an absorbing liquid (1 mm DCM: t=0.1 @24keV). This is where the very different behaviour of neutrons towards matter represents an advantage[7]. By exploiting the evanescent wave in a grazing incidence small angle neutron scattering (GISANS) experiment, the highly scattering electrolyte can be used as the interface for total reflection of the neutron beam which impinges through the back of the sample. This way, any absorption or parasitic scattering from the electrolyte is kept to a minimum. Additionally, possible side reactions that could emerge by the use of high energy X-rays (photoelectrons) will not occur and hence not disturb the electrochemistry.

## Experimental results



| Material | Density [g/cm$^3$] | SLD (Re) [$10^{-6}$ Å$^{-2}$] |
|---|---|---|
| Silicon | 2.2 | 2.074 |
| Silica | 2.2 | 3.475 |
| TiN | 5.22 | 3.043 |
| $Bi_2Te_3$ | 7.74 | 1.985 |
| $CD_2Cl_2$ | 1.36 | 3.688 |

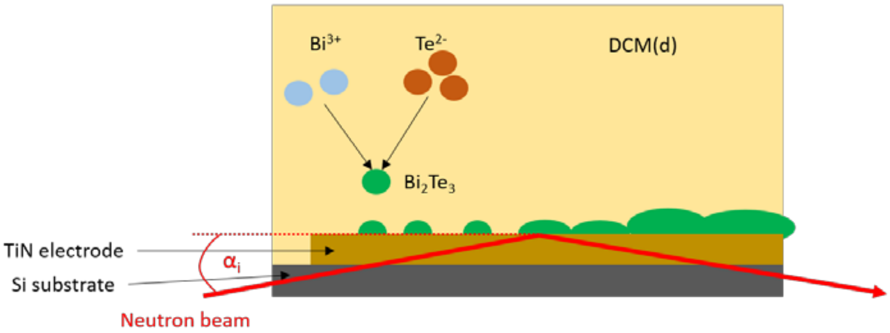


*Figure 1: Material density, scattering length density (SLD) of the employed materials (left) and schematic drawing (right) of the setup designed for the in situ GISANS experiments.*

**Figure 1** shows the calculated contrast values for the materials employed in this experiment as well as the used geometry. As stated above, the beam penetrated the sample through its back (Si, 5 mm thick) in order to probe the electrode surface (TiN, 200 nm) on which $Bi_2Te_3$ was deposited. A potential of -2 V versus Ag/AgCl was used for electrodeposition, which was applied for 1,2,1,70,… seconds after which SANS collections of 1 h were done at a wavelength of 7 Å and sample detector distance of 6.7 m.

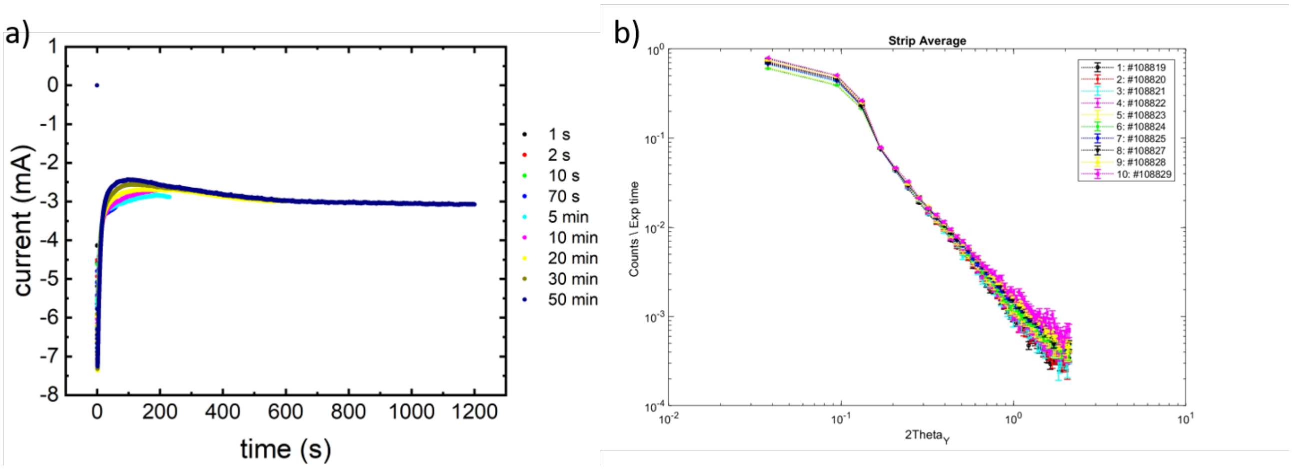


*Figure 2: Current transients of the consecutively applied potential of -2 V during bismuth telluride deposition.*

**Figure 2 a)** shows the transients of consecutive steps during electrodeposition at -2 V, with the Yoneda cuts from the SANS images shown in **Figure 2 b)**. The first shows the very good reproducibility of electrochemistry as the transients all have very similar shapes. The latter shows that $Bi_2Te_3$ deposits layer-by-layer as opposed to island growth, as no lateral peaks are visible which would indicate a correlation distance between growing islands. We can see increasing intensity in the high q-range, which is most probably related to increasing roughness of the film as it becomes thicker. This still has to be confirmed by SEM.

## Ongoing work

The data will be fully reduced and additional SEM and XRR measurements will be done to fully explain the happenings in this system. If suitable, BornAgain simulations of the SANS data will be done and included in the final report. Ultimately, the data from this experiment is planned to be part of a publication on Bismuth Telluride deposition with Robert Cubitt as co-author.

**1** Ustarroz, J. *et al. Electrochem. commun.* 13, 1320–1323 (2011)

**2** Ruge, M. *et al. Phys. Rev. Lett.* 112, 1–5 (2014)

**3** Dupont, M. F. *et al. J. Electrochem. Soc.* 162, A1809–A1815 (2015)

**4** Schwartzkopf, M. *et al. Nanoscale* 5, 5053 (2013)

**5** Kaune, G. *et al. ACS Appl. Mater. Interfaces* 1, 353–360 (2009)

**6** Reichert, H. *et al. Phys. B Condens. Matter* 336, 46–55 (2003)

**7** Nouhi, S. *et al. J. Appl. Crystallogr.* 50, 1066–1074 (2017)