Experiment Report Form

ESRF	**Experiment title:** Structure, Shape and Epitaxy of Supported Magnetite Nanoparticles	**Experiment number**: CH6361
Beamline: BM-32	**Date of experiment**: from: 31.01.23 to: 07.02.23	**Date of report**: 23.02.2023
Shifts: 18	**Local contact(s)**: MARTINELLI Lucio, RENAUD Gilles, DE SANTIS Maurizio	*Received at ESRF:*

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Report:

We investigated the growth of magnetite nanoparticles on Al_2O_3 (0 0 0 1) substrate by reactive physical vapor deposition of iron into an oxygen atmosphere. In the first step, the effect of temperature and deposition time of iron on the growth of magnetite was investigated. Temperature was varied from 300 to 700°C in order to grow epitaxial nanoparticles (NPs) with strong facet signal to monitor the CTR changes before and after dosing formic acid. Based on the thermodynamic point of view, elevating the temperature leads to the formation of larger nanoparticles with respect to the Wolff rearrangement. The growth temperature of 450°C was followed for further characterization as an optimum target temperature since no iron-oxide-related reflections were detected at the higher temperature (700°C). It is worth mentioning that the reflectivity results on the prepared sample at 700°C didn't represent the acceptable thickness/features for the deposited layer. A similar observation was obtained for the prepared sample at Nanolab at DESY. The growth interpretation of magnetite NPs at high temperatures and the propensity of evaporated substances' interaction with the substrate still demand further characterization.

In-situ growth of magnetite nanoparticles on the sapphire support was studied at 300 and 450°C by performing the inplane rocking scans during the growth. To this end, different inplane reflections of magnetite and hematite were selected to monitor the orientation and phase structure of the nanoparticles during the growth. Based on the evolution of the inplane scans through the deposition, it can be concluded that the crystalline structure of magnetite NPs initiated to form instantly after the deposition by recovering the pressure inside the MBE chamber (after closing the oxygen valve and evaporator shutter) since in the middle of the deposition, only a slight increase in 2 2 0 reflection of magnetite is perceived (**Figure 1**). The possibility of hematite formation was also taken into account, seeking the inplane rocking scans over the 1 1 0 and 3 0 0 reflections of this phase. The emergence of 60 repeated reflection peaks at 2θ=35.49 [Hematite (3 0 0))] informs that hematite phase can also exist in the nanoparticle structure at room temperature. In other words, the final structure of nanoparticles consists of magnetite and hematite, while magnetite is the dominant phase in the NPs' structure.

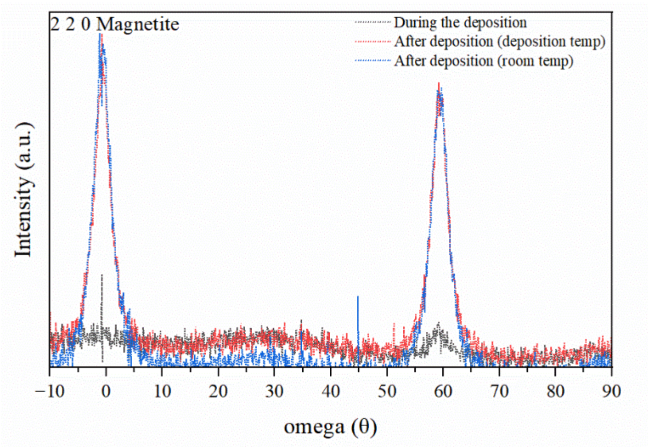

Figure 1. In-plane rocking scan in search of 2 2 0 reflection of Magnetite, during, and After the deposition.

At room temperature, the crystalline structure of the developed NPs was studied using the in-plane rocking/radial scans. Results demonstrated the formation of 1 1 1 oriented magnetite NPs on the sapphire substrate. The effect of formic acid adsorption on (1 1 1) surface of magnetite NPs was probed by candidating the different rods based on our published paper on single crystal magnetite[1]. Formic acid was dosed up to 10 L in one step to saturate the surface. **Figure 2** illustrates the CTRs evolution before and after dosing formic acid. The slight change between the Bragg peaks suggests the near-surface changes taking place on 1 1 1 facet. This can correlate to surface roughening originating from the adsorb formic acid.

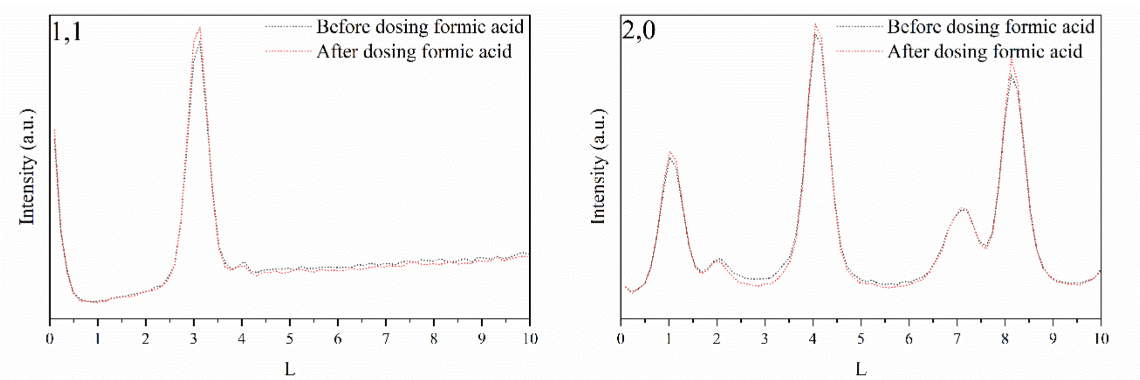

Figure 2. CTR measurements (in surface coordination system) before and after dosing formic acid (10L) at room temperature.

References:

[1] Creutzburg, M., Sellschopp, K., Gleißner, R., Arndt, B., Vonbun-Feldbauer, G.B., Vonk, V., Noei, H. and Stierle, A., 2022. Surface structure of magnetite (111) under oxidizing and reducing conditions. *Journal of Physics: Condensed Matter*, *34*(16), p.164003.