

Electron induced fragmentation and deposit formation from nano-meter thin surface layers of $\text{HFeCo}_3(\text{CO})_{12}$ adsorbed on gold surfaces.

Oddur Ingólfsson*¹, Ragesh Kumar T P*², Ilyas Unlu³, D. Howard Fairbrother¹ and Sven Barth³¶

* Science Institute and Department of Chemistry, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland

¹ Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States

³ TU Wien, Inst. of Materials Chemistry, Getreidemarkt 9/BC/02, A-1060 Wien, Austria.

Synopsis In the current contribution, we present electron induced fragmentation and deposit formation from nano-meter thin surface layers of $\text{HFeCo}_3(\text{CO})_{12}$ adsorbed on gold surfaces and exposed to high-energy (400 eV) electrons from a flood gun.

There is an increase in demand for developing and improving the efficiency of techniques that are capable of fabricating sub-10 nm structures in a controlled manner. Focused electron beam induced deposition (FEBID) [1,2] is a technique with this potential and the capability of fabricating direct 3D-nanostructures on top of almost any substrate irrespective to its geometry. In FEBID, a high-energy electron beam is focused onto a substrate on which precursor molecules are adsorbed at constant partial pressure. The precursor molecules dissociate under exposure to the electron beam, apparently through interaction with low energy secondary electrons produced through the interaction of the primary beam with the surface [3]. Ideally the precursor decomposes completely and volatile ligands are pumped away while the non-volatile fragments (metal) deposits to grow the desired nanostructures. However, FEBID is still facing challenges such as lateral broadening of structures and impurities in the deposit from incomplete decomposition of the precursor molecules.

$\text{HFeCo}_3(\text{CO})_{12}$ is the first single-source heteronuclear precursor molecule used in FEBID to fabricate bimetallic nanostructures and it was shown that 80% pure FeCo deposits could typically be attained [4], a purity much higher than normally attainable. In an attempt to better understand the mechanisms behind the decomposition of this precursor we recently conducted a gas phase study on the energy dependency of dissociative electron attachment (DEA) and dissociative ionization (DI) of this molecule [5, 6]. It shows rich fragmentation through both DEA and DI and These experiments give valuable information on the potential fragmentation mechanisms involved in its deposition process, however, no information on the role of the surface interaction can be obtained in these experiments.

In the current contribution, we present electron induced fragmentation and deposit formation from nano-meter thin surface layers of $\text{HFeCo}_3(\text{CO})_{12}$ adsorbed on gold surfaces and exposed to high-energy (400 eV) electrons from a flood gun. Here, desorbing fragments are monitored by mass spectrometry,

while the electron dose dependence of the deposit composition, is monitored by means of X-ray photo electron spectroscopy (XPS). As expected the predominant desorption, monitored with mass spectrometry, is that of CO. Correspondingly a rapid reduction of the CO content is observed at the surface. This is followed by decomposition of the remaining CO and an apparent iron oxide formation. Hence, based on our preliminary analysis of the development of the electron dose dependency of the XPS peak areas, and peak positions, electron induced decomposition of $\text{HFeCo}_3(\text{CO})_{12}$ proceeds in two steps. In the first step, with electron dose of $<5 \times 10^{16} \text{e}^-/\text{cm}^2$, the peak area analysis shows an average 9 CO lost per molecule. The second step proceeds considerably slower and constitutes decomposition of the remaining CO and the apparent conversion iron into iron oxide. Furthermore, by increase the substrate temperature from the initial -60 °C to RT (25 °C), all remaining CO is removed from the surface. This observation is consistent with the high purity of FeCo deposit in FEBID from $\text{HFeCo}_3(\text{CO})_{12}$

In the current contribution, we compare the electron induced reaction of $\text{HFeCo}_3(\text{CO})_{12}$ adsorbed on gold surfaces with previous gas phase studies and FEBID using $\text{HFeCo}_3(\text{CO})_{12}$ as precursor

Acknowledgments: This work was supported by Icelandic Centre for Research (RANNIS) and the University of Iceland Research Fund. RKTP acknowledges financial support through a PhD grant from the University of Iceland Research Fund and a from CELINA for a short term scientific mission.

References

- [1] I. Utke *et al.* 2008 *J. Vac. Sci. Technol. B*: **26**, 1197.
- [3] M. Thorman *et al.* 2015 *Beilstein J. Nanotechnol.*, **6**, 1904-1926, and references therein.
- [4] F. Porrati *et al.* 2015 *Nanotechnol.* **26**, 475701.
- [5] T P. R *et al.* 2016 *EPJ D*, **70**, 163.
- [6] T P. R *et al.*, 2017 *Submitted*