

The fate of metalorganic molecule ligands in e-nanoprinting

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Gas-assisted focused electron beam induced deposition (FEBID) in scanning electron microscopes is a powerful direct-write e-nanoprinting approach for prototyping three-dimensional nanostructures with large shape variety at nanometer-scale resolution [1]. It employs electron induced dissociation of surface adsorbates continuously supplied via a gas injection system. A longstanding challenge is to obtain clean metal deposits, i.e. the organometallic molecules must be fully stripped off their ligands via electron irradiation. A great deal of insightful fundamental research was performed to understand the electron induced dissociation mechanisms of such molecules in the community, see [2] for example. More recently, the focus widened to surface kinetic mechanisms [3] which act at the surface adsorption stage of the pristine molecule as well as to the desorption behavior of detached ligands after adsorbate dissociation. An overview of mechanisms is shown in fig. 1 together with their potential to result in metal-rich or "ligand"-rich e-nanoprint material. This contribution will give a summary of these and highlight ligand co-dissociation as one specific mechanism, see fig. 2. Related continuum modelling yields novel important FEBID scaling laws in terms of inherent characteristic time periods which can be addressed by electron beam exposure times, electron flux, and substrate temperature [4].

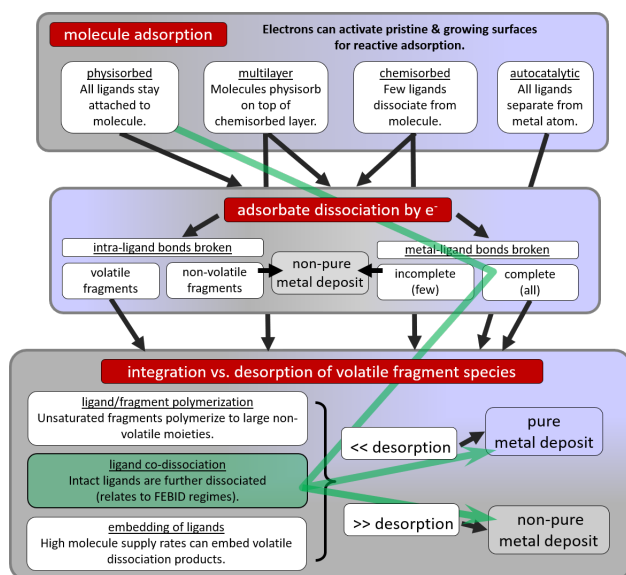


Figure 1. Mechanisms and reactions a precursor molecule can undergo during electron-induced nanoprinting. Blue shading means clean metal, grey shading carbon rich (low metal content) material. Modified from [3]. The green arrow depicts the ligand co-dissociation scenario shown in fig. 2.

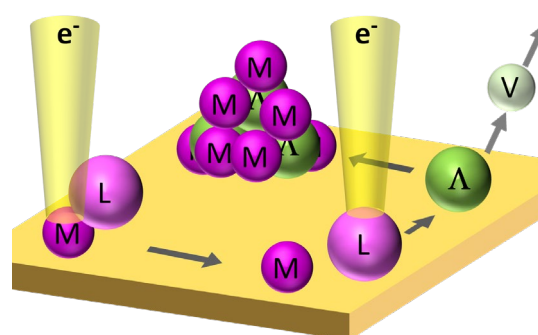


Figure 2. Schematic representation of the ligand co-dissociation scenario depicted in figure 1 (green arrow). The metal-organic precursor molecules are injected by a gas injection system into a scanning electron microscope and physisorb on the substrate surface. For modelling, the molecules are generically represented by the metal atom M and an organic ligand L. They dissociate in the focus spot under electron irradiation into a non-volatile metal-containing fragment M and a detached ligand L. The detached ligand L either desorbs entirely or dissociates into a non-volatile residue Λ and a volatile part V [4]. The final deposit material composition is then $M_x\Lambda_{1-x}$.

References

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