Jakub Mateusz Jurczyk

Solid State Physics Department

Abstract of the doctoral thesis: “Study of novel precursors for Focused Electron Beam Induced Deposition of Metal Nanowires”

Recent development of nanotechnology created a need to introduce reliable and reproducible methods of fabrication of structures in nanoscale. Focused electron beam induced deposition (FEBID) is a nano-structuring method, which allows for direct, mask-less deposition of three-dimensional, vertical structures with spatial resolution below 20nm, reaching even single nanometers. Direct approach and versatility are the main advantages of FEBID, thanks to which it was applied in various different fields, including nano-magnetism, plasmonics, manufacturing of sensor nano-devices or scanning probe microscopy tips or correction of lithography masks. Despite its advantages and various applications, there is still a lot of unresolved challenges concerning deposition with focused electron beam. The most prominent are the low metal content of deposited structures, coming mostly from using metalorganic (or organometallic) compounds to deposit metal or so-called proximity effects, which lower lateral resolution of the deposits.

This PhD Thesis addresses these challenges by presenting the results of systematic investigation of various novel metalorganic compounds as potential precursors for FEBID. The precursors are coming from three groups of complexes: silver carboxylates $Ag_2(\mu\text{-}O_2CC(Me)_2Et)_2$, $Ag_2(\mu\text{-}O_2C^tBu)_2$, $Ag_2(\mu\text{-}O_2CCF_3)_2$, $Ag_2(\mu\text{-}O_2CC_2F_5)_2$, $Ag_2(\mu\text{-}O_2CC_3F_7)_2$, ruthenium heteroleptic complexes $Ru(\eta^3\text{-}C_3H_5)(CO)_3Br)$, $Ru(CO)_4Br_2$ and halogenated N-heterocyclic carbene compounds $Au(NHC)Me_2Cl$, $Au(NHC)Et_2Cl$. Chemical compositions of deposits obtained with silver carboxylates spanned from 34 at.% for $Ag_2(\mu\text{-}O_2CC_3F_7)_2$ up to 76 at.% for $Ag_2(\mu\text{-}O_2CC_2F_5)_2$. FEBID with ruthenium complexes resulted in metal contents around 23 at.% and with gold compounds not more than 16 at.%. TEM measurements have proven that for both Ag and Ru FEBID, the bonds between metal atoms and ligands have been successfully cleaved. Metal contents of Ru-containing structures were later enhanced with a forming gas based post-purification, which allowed for obtaining even 83 at.% of Ru without destroying the integrity of the deposit.

Important part of this PhD Thesis are characterisation methods. The thesis contains a first application of vacuum thermogravimetry as a method of pre-screening of thermal properties of low-volatility silver compounds. Secondly, focused electron beam induced mass spectrometry (FEBiMS) as a novel method to investigate volatile charged species leaving material due to irradiation with electrons was developed here. It was used to examine three solid compounds: $Ru_3(CO)_{12}$, $Ag_2(\mu\text{-}O_2CC_2F_5)_2$, $Cu_2(\mu\text{-}O_2CC_2F_5)_4$ and one gaseous compound adsorbed to the surface of the sample with constant gas supply: $W(CO)_6$. These both methods are novel in the field of FEBID and provide new, important insight into thermal properties of precursor and the interaction between physisorbed precursor molecules and electron beam. Furthermore, WDS combined with EDX for elemental composition was developed as characterization for overlapping spectral peaks. TEM was used for establishing crystal structure, AFM for thickness determination of deposits and four-point probe method - for electrical resistivity measurements.

The last part of the thesis focuses on the development of FEBID modelling. It consists of two parts, first being the extension to characteristic rate (frequency) maps by introducing the shape resolution parameter and the surface diffusion rate. Second part considers modelling of co-deposition of ligands and its influence on metal content in the deposit. The model will be confronted with experimental results showing qualitative agreement between calculations and experiments.

Kraków 07.07.2021