Ph.D. Course in Materials Science and Nanotechnology

University of Milano-Bicocca, Department of Materials Science, via Cozzi 55, 20125 Milano

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Seminar room - Department of Materials Science U5

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Atomic layer deposition of cobalt phosphate thin films for the oxygen evolution reaction

Electricity storage into chemicals is an attractive solution to the challenge of the intermittency of renewable energy sources, such as wind and solar. The most known example is water splitting, where since a few years cobalt phosphate is acknowledged as reliable alternative to noble metal-based electrocatalysts, specifically for the oxygen evolution reaction (OER). So far, the preparation of cobalt-phosphate-based electrocatalysts has been largely limited to (photo)electrodeposition in solution, implying that the control of the thickness is strongly related to the control of the current applied for the preparation of the electrocatalyst, and the composition is influenced by precursors, electrolytes and pH. A higher level of control over material composition can be achieved using atomic layer deposition (ALD). ALD, a thin film deposition method based on the cyclic sequential dosing of gas-phase reactants, is a key technology for the preparation, nanostructuring and engineering of thin films in the research for energy applications, ranging from solar cell technologies to water splitting and fuel cells. Characteristic features of ALD include excellent control of the thickness at atomic level, good uniformity and conformality and high control over the material composition.

In this work plasma-assisted ALD of cobalt phosphate has been performed by combining ALD of CoO_x from cobaltocene and O_2 plasma as co-reactant, with cycles of trimethyl phosphate followed by O_2 plasma exposure, according to an ABCD recipe scheme. For the CoO_x part (AB) we adopted the recipe reported by Donders et al. Instead, the adoption of TMP exposure followed by O_2 plasma (CD) has not been reported yet in the literature.

The ALD process shows linear growth with no nucleation delay on silicon with native oxide and a growth per cycle of 1.12 ± 0.05 Å at 300^{O}C. The ALD saturation behavior has been demonstrated for each dosing step and the process shows negligible inhomogeneity in terms of film thickness (1.0%) and refractive index *n* (0.5%) over an area of 78.5 cm^2. The opto-chemical properties of cobalt phosphate layers have been characterized in the range of deposition temperature between 100^{O}C and 300^{O}C. Furthermore the reaction mechanism during ALD has been elucidated by time-resolved quadrupole mass spectrometry measurements.

The developed electro-catalyst is active towards OER and outperforms traditionally electro-deposited films. Moreover, we report on the superior quality of ALD cobalt phosphate in terms of low content of impurities when compared to the commonly adopted

electrodeposition method and on the opportunity of tuning the Co-to-P ratio by combining the cobalt phosphate process with extra ALD cycles of CoO_x.