UNIVERSITY of HOUSTON

MATERIALS ENGINEERING PROGRAM

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Zoom link: https://us02web.zoom.us/j/85209776614 (ID: 852 0977 6614)

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Ph.D. Dissertation Defense

Advisor: Dr. Stanko R. Brankovic

**Electrochemical Synthesis of Functional Films and Surfaces**

This dissertation represents experimental work with significant analytical modeling in areas of electrochemical material science and thin films. It produces several fundamental results with great implications for practitioners in the field and various applications in technological enterprises. The dissertation addresses problems in a broad range of electrochemical synthesis methods, including stress control in the electrochemical deposition of functional films, synthesis of functional surfaces, and monolayer deposits.

Thin-film residual stress developed during the deposition can adversely affect the film's reliability and functionality. This research describes the origin of the crack formation in Cr and Pd films, two industrially significant coatings, using *in-situ* stress measurement during and after the film deposition as the primary experimental approach. Our finding in chromium electrodeposition from Cr(III) electrolytes relates the origin of cracks to the formation and subsequent decomposition of Cr-H. Employing various experimental methods, data analysis, and modeling, the research describes the design of effective PCD (pulse-currents-deposition) that reduces Cr-H accumulation, the stress generating source, at the deposition stage. The designed PCD with $\frac{t_{on}}{t_{off}} > 5$ where $t_{on} > 1$ showed drastic crack mitigation in the deposits. Additionally, this work investigates stress development during Pd film deposition and shows that introducing $Pb^{2+}$ ion in the depositing electrolytes can lead to Pb underpotential co-deposition as Pd-Pb intermetallic, which suppresses the generated stress from hydrogen absorption.

This dissertation also demonstrates electrochemical techniques for electroless Pb ML deposition and surface decoration as a practical approach for designing chemical sensors and developing new deposition processes like e-less ALD (atomic-layer-deposition). First, it presents a novel chemi-resistive hydrogen-sulfide sensor, designed and synthesized by atomic-layer surface modification. The modification with AuPd alloy improves chemi-resistivity of Au ultra-thin film and results in fast, reproducible, and linear sensing for hydrogen-sulfide from aqueous environments. Further, this research discusses an analytical study on the electroless Pb ML deposition on various substrates. The analysis shows that the surfaces' electronic nature and catalytic phenomena are the main factors in electroless ML deposition. These findings have significance for electrochemical deposition on nano features and shed light on a pathway to synthesize core-shell nano-catalysts using a new e-less ALD method.