Electrodeposition of nanostructured metals on silicon. A focus on the rhodium/n-doped silicon composite as a promising platform for energy applications

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Significance and Relevance

The work demonstrates the successful electrodeposition of nanostructured metals, with a focus on rhodium, on n-doped silicon. High surface coverage (up to 84%), tunable particle sizes (57-168 nm) and controlled morphology were achieved using multi-cycle charge-controlled deposition. Rhodium electrodeposition on silicon is scarcely reported in the literature and these results could improve applications in energy-related fields, including catalysis for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water splitting devices.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors and sustainable and clean energy production and transport

Preferred presentation: Poster

Introduction and Motivations

In light of the escalating energy crisis and environmental concerns, there is an urgent need for clean and sustainable energy-related materials and related storage and conversion devices[1]. The deposition of thin metal films or patterns and nanostructured metal materials on silicon substrates holds significant technological importance as it offers a unique opportunity to blend the advantageous characteristics of metals with the exceptional electronic properties of silicon. This combination is pivotal for developing advanced technologies in energy storage, hydrogen production, catalysis, photovoltaics, and sensing[2]. To achieve this object the electrodeposition technique was selected. The advantage of this technique over others such as physical vapor deposition (PVD) or chemical vapor deposition (CVD), at the state of art, is that it is performed at room temperature and atmospheric pressure in aqueous solution, making it inexpensive and easily scalable[3].

Results and Discussion

The initial selection of metals for the electrodeposition on the silicon substrate was conducted through the study of the data obtained from computational calculations thanks to The Open Quantum Materials Database (OQMD) based on Density Functional Theory (DFT) at the PBE/PAW level. Voltammetric studies were then carried out using solutions containing Ni, Ru, Pd, Rh, Pt, Ag, Mn, and Co. Charge-controlled depositions were performed, and tests on electroless deposition were made. The deposits obtained were characterized morphologically and compositionally using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy Analysis (EDS).

Following this preliminary study rhodium turned out to be the most promising metal among those selected according to the characterization accomplished.

Focusing on rhodium electrodeposition a high surface coverage (up to 84%), tunable particle sizes (57-168 nm) and controlled morphology were achieved using multi-cycle charge-controlled deposition. Additionally, X-ray Photoelectron Spectroscopy (XPS) demonstrated the presence of a rhodium deposit in a purely metallic form. The advances presented in this work address a notable gap in the literature on rhodium electrodeposition on silicon and offer significant potential for energy-related applications. For instance, a rhodium-silicon platform could be significant for HER catalysis as reported in the literature[4], since it separates hydrogen adsorption (on Rh) and desorption (on Si), overcoming Sabatier's principle limitations and achieving higher efficiency and stability than platinum-based catalysts at high current densities.

Obtaining a silicon surface with a higher surface area might be useful for future developments to enhance its catalytic activity.

Therefore the knowledge gained was used to realize ultrathin silicon nanowires (NWs) using a procedure, at the state of the art, not widely used in the literature consisting in a wet etching process assisted by an electrochemically deposited metal thin film.

By providing an efficient, scalable, and cost-effective alternative to traditional vapor-phase methods, this work paves the way for the building up of composites presenting enhanced catalytic performance in various hydrogen fields, such as the hydrogen evolution reaction (HER), contributing to the development of sustainable energy.

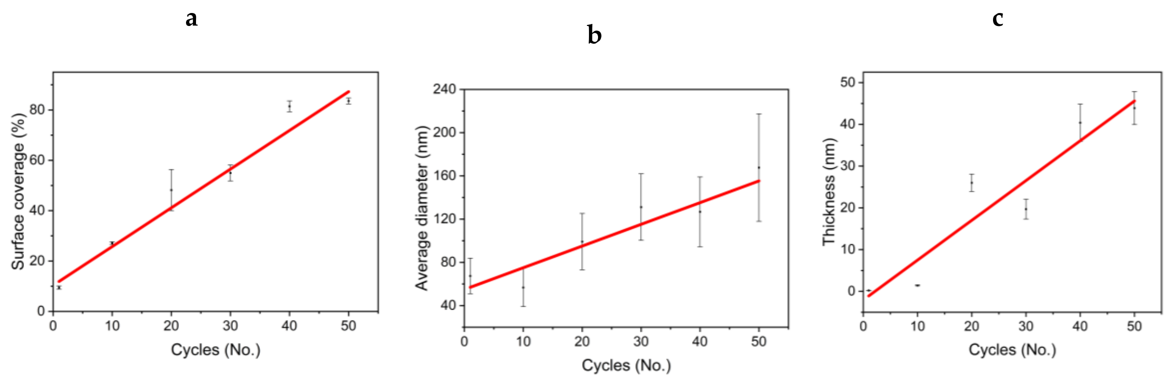

Figure 1: a) Surface coverage trend; b) average particles diameter size trend; c) equivalent thickness trend of the deposits, obtained through a variable number of charge controlled deposition cycles (1, 10, 20, 30, 40, and 50 cycles) on Si working electrode using H_2SO4 0.1 M, $RhCl_3$ 1mM solution.

References

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