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Extended abstract

EXTENDED ABSTRACT

Epitaxial growth by monolayer-restricted galvanic displacement•

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Abstract: The development of a new method for epitaxial growth of metals in solution by galvanic displacement of layers pre-deposited by underpotential deposition (UPD) was discussed and experimentally illustrated throughout the lecture. Cyclic voltammetry (CV) and scanning tunneling microscopy (STM) were employed to perform and monitor a "quasi-perfect", two-dimensional growth of Ag on Au(111), Cu on Ag(111), and Cu on Au(111) by repetitive galvanic displacement of underpotentially deposited monolayers. A comparative study emphasizes the displacement stoichiometry as an efficient tool for thickness control during the deposition process and as a key parameter that affects the deposit morphology. The excellent quality of the layers deposited by monolayer-restricted galvanic displacement was manifested by steady UPD voltammetry and ascertained by the flat and uniform surface morphology that was maintained during the entire growth process.

Keywords: underpotential deposition; crystal growth; surface morphology; STM.

Epitaxial growth by monolayer-restricted galvanic displacement is realized utilizing a concept for submonolayer to monolayer surface modification assisted by the irreversible galvanic displacement of an underpotentially deposited (UPD) less-noble metal by a more-noble metal.[1] This protocol functions in homo- and hetero-epitaxial systems where the displaced UPD metals are displaced not only on the substrate, but also on the growing metal of interest; hence, the "building block" reaction could be repeated as many times as desired. Similar pathways have been technically employed in electrochemical atomic layer epitaxy (EC ALE) for the growth of epitaxial compound semiconductor layers with a wide spectrum of applications in the electronics industry.[2] The electroless nature of the

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displacement reaction allows for decoupling of mutually dependent growth controlling factors in a typical electrodeposition scenario, thus improving the overall deposition control.

The development of a new method for hetero-epitaxial growth by monolayer restricted galvanic displacement was presented in the lecture. Although the epitaxial growth of Ag on Au(111) was the system under detailed consideration, complementary results for Cu epitaxial growth on Ag(111) and on Au(111) suggest that this method can be applied to a number of other systems. The main limitation of the proposed method is manifested by the requirement that the selected underpotentially deposited metals have to feature UPD on both the substrate and the growing metal. The newly developed method for epitaxial growth of thin films enables the substrate with a metal underpotentially deposited on it to be transferred into a solution that contains ions of a more noble metal than the UPD metal. A naturally ensuing galvanic displacement results in stoichiometric exchange between the UPD atomic layer and the metal ions of interest. This building block reaction can be repeated as many times as desired. The unique property that warrants success of the proposed strategy is associated with the fact that UPD is a reversible process and galvanic displacement is not. Therefore, a metal that displaces the UPD layer remains on the surface awaiting another layer "to come" in the next cycle. The continuous accumulation of new epitaxial layers eventually results in a thin epitaxial film with perfectly controlled thickness. The driving force for the displacement step is the formation of the corrosion potential between the UPD metal and the substrate.

Kinetic factors that govern the feasibility of the described procedure and provide hand-on knowledge for precise control of the growth are associated with the stability of an underpotentially deposited metal layer at the open circuit potential (OCP). A comprehensive kinetic study performed during this work identified oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and nitrate electroreduction as typical oxidizing agents that compete with the displacing metal ions in any working environment.[3] The completed kinetic study served as a base for the development of an analytical model. Assuming Langmuir and/or Frumkin type UPD behavior, the derived equation enables a quantitative prediction of the stability of the UPD layer at the OCP and precise kinetics control of the galvanic displacement based on readily measurable experimental parameters. A fitting of the experimental results for the systems Pb/Cu(111) and Pb/Ag(111) with the model equation showed an excellent prediction of the stability of the UPD layer at the OCP and renders the model applicable for a variety of kinetic studies.[4]

The most important result of this research is manifested by work focused on initial trials, procedure optimization, a stoichiometric study and the successful implementation of the galvanic displacement as a tool for epitaxial thin film

growth.[5,6] Furthermore, both qualitative and quantitative examination of deposited thin films ascertained the applicability of the proposed strategy in metal epitaxy. A systematic study of thin film morphology as a function of the oxidetion state of the UPD metal suggested growth of Ag by displacement of a Tl UPD layer (1:1 displacement) as preferred, considering the surface roughness and uniformity. Subsequent stripping experiments validated the proposed working formula for galvanic displacement that takes into account not only the stoichiometric arguments, but also the crystallographic parameters of the participating elements. High-resolution X-ray photoelectron spectroscopy (XPS) experiments suggested not even a trace of Tl and Pb was present in the respectively grown Ag layers, thus confirming the purity of the deposit. At the same time, the surface confined intermixing between Ag and Bi, undoubtedly demonstrated by CV and XPS, could be envisioned as a fundament of the new strategy for the deposition of multi-functional ordered surface alloys (Ag–Bi, Au–Bi and Pt–Bi) with immediate application in fuel cell catalysis.[7] The results obtained for the Cu/Ag(111) and Cu/Au(111) systems prove epitaxial growth by monolayer restricted galvanic displacement as a viable method for obtaining epitaxial thin films of excellent quality.[8] The long term fundamental goals of presented research are related to the implementation of monolayer restricted galvanic displacement to other systems, such as Au/Pt(111), Ag/Pt(111), Pd/Pt(111), and further expansion towards the growth of "perfectly layered" metal composites.

И З В О Д

ЕПИТАКСИЈАЛНИ РАСТ КРИСТАЛА ПРИМЕНОМ МЕТОДЕ ГАЛВАНСКЕ ИЗМЕНЕ ОГРАНИЧЕНЕ НА МОНОСЛОЈ

РАСТКО ВАСИЛИЋ

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У овом предавању су приказане основне идеје и резултати примене нове методе епитаксијалног раста кристала галванском изменом ограниченом на монослој. Метода је заснована на спонтаном, иреверзибилном, редокс процесу при коме се подпотенцијално депоновани слој замењује слојем (електрохемијски) племенитијих металних јона из раствора, који се редукују на кристалној површини. У одређеном броју система, понављање овог корака резултира формирањем танких филмова који прате морфологију субстрата. Представљени су резултати добијени за систем Ag/Au(111), Cu/Ag(111) и Cu/Au(111). Посебна пажња је посвећена испитивању утицаја стехиометрије галванске измене у систему Ag/Au(111), када је подпотенцијално депоновани слој формиран од атома Tl, Pb и Bi, редом. Карактеризација овако добијених танких филмова показује да се методом галванске измене ограничене на монослој стиче максимална контрола униформности раста уз минимум спољашње контроле. Танки епитаксијални филмови добијени на овај начин су супериорни у односу на танке филмове добијене уобичајеним техникама електродепозиције.

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