Final report for project ÅF 22-150

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Towards multiscale design of thin-film materials

The ÅF 22-150 project encompasses both experimental and theoretical aspects that aims at establishing the framework for facilitating multiscale design of thin-film materials. The project resulted in **eight published articles**, while another **six articles are under review/in final preparation**. The highlights and key outcomes of the project are presented in the following.

Fundamental studies of metal film growth on weakly-interacting substrates

We demonstrated a versatile concept for manipulating morphology of thin (≤25 nm) noble-metal films on weakly interacting substrates using growth of Ag on SiO2 as a model system. The concept entails deployment of minority metallic (Cu, Au, Al, Ti, Cr, and Mo) alloying species at the Ag-layer growth front. Data from in situ and real-time monitoring of the deposition process guided us to deploy alloying species with high temporal precision to selectively target growth stages before and after coalescence completion. Pre-coalescence deployment of all alloying agents yielded a more pronounced 2D growth morphology, which for the case of Cu, Al, and Au was achieved without compromising the Ag-layer electrical conductivity. A more complex behavior was observed when alloying atoms are deposited during the post-coalescence growth stages: Cu, Au, Al, and Cr favor 2D morphology, while Ti and Mo yield a more pronounced three-dimensional morphological evolution. The overall results of this work showed that targeted deployment of alloying agents constitutes a generic platform for designing bespoken heterostructures between metal layers and technologically relevant weakly interacting substrates.

We also studied the effect of nitrogen on the morphological evolution of thin silver (Ag) films deposited on weakly-interacting amorphous carbon (a-C) and silicon oxide (SiO_x) surfaces. We synthesized films by direct current magnetron sputtering (DCMS), high power impulse magnetron sputtering (HiPIMS), and electron-beam evaporation (EBE). We monitor growth in situ and in real time by measuring the evolution of film stress and optical properties, complemented by ex situ analyses of discontinuous-layer morphologies, film crystal structure, and film composition. We found that addition of molecular nitrogen (N2) to the plasmagenic gas (Ar) during DCMS and HiPIMS promotes a two-dimensional (2D) morphology. Concurrently, EBE-deposited films exhibit a significantly more pronounced three-dimensional morphological evolution, independently from the gas atmosphere composition. We concluded that the 2D morphology in DCMS- and HiPIMS-grown films is enhanced due to incorporation of atomic nitrogen (N)—result of plasma-induced N2 dissociation—that hinders island reshaping during coalescence. This mechanism is not active during EBE due to the absence of energetic plasma electrons driving N2 dissociation. The overall results of the study showed that accurate control of vapor-phase chemistry is of paramount importance when using gaseous species as agents for manipulating growth in weakly-interacting film-substrate systems.

This part of the project was complemented by studies on the effect of impurities on the morphological evolution of thin silver (Ag) and copper (Cu) films deposited by direct current and high-power impulse magnetron sputtering on weakly-interacting silicon dioxide and amorphous carbon substrates. We systematically varied the ratio of impurity-to-metal particle arriving at the substrate and assessed the character of film morphological evolution and the overall growth dynamics by means of real-time in-situ diagnostic tools and ex-situ analyses. We found that both thin-film materials exhibit a three-dimensional morphological evolution, which for the case of Ag is governed by the effect of metal vapor flux magnitude on the dynamic competition among island nucleation, growth, and coalescence (*vapor-controlled growth regime*). Cu exhibits a similar (vis-à-vis Ag) behavior with respect to the overall morphology and impurity for relatively low impurity fluxes. Above a certain flux threshold, however, the impurity content in the Cu layers increases sharply and film morphological evolution is seemingly determined by the effect of impurities on the fundamental structure-forming process of island nucleation, grain growth, and crystal growth (impurity-controlled growth regime). The overall results presented herein show that impurities are a key material-dependent factor that needs to be considered when designing morphologies of or studying growth dynamics in weakly-interacting film-substrate systems.

The results of our investigations led to the following publications:

Article 1
A. Jamnig, N. Pliatsikas, G. Abadias, and **K. Sarakinos**, "Manipulation of thin metal film morphology on weakly interacting substrates via selective deployment of alloying species", J. Vac. Sci. Technol. A 40 (2022) 033407. (https://doi.org/10.1116/6.0001700)

Article 2
K. Sarakinos, D. Babonneau, J. Ramade, Y. Robin, K. Solanki, K. Mizohata, V. Tuboltsev, N. Pliatsikas, B. Krause, and G. Abadias, "Unravelling the effect of nitrogen on the morphological evolution of thin silver films on weakly-interacting substrates", Appl. Surf. Sci. 649 (2024) 159209. (https://doi.org/10.1016/j.apsusc.2023.159209)

Article 3
K. Sarakinos, S. Kirjonen, B. Sanzone, F.L. Nadji Adjim, A. Ashraf, N.J. Tanzum, S. Moraes, S. Korkos, and K. Mizohata, "Vapor-and impurity-controlled growth regimes during deposition of thin noble metal films on weakly-interacting substrates", Surf. Coat. Technol. 505 (2025) 132111. (https://doi.org/10.1016/j.surfcoat.2025.132111)

Nanoscale design of complex alloys

We studied the structure formation in thin epitaxial nickel-aluminum (an important alloy for e.g., turbine blades) films ($Ni_{1-x}Al_x$; Al atomic fraction x up to x = 0.24) grown on MgO(001) substrates by magnetron sputtering. Experimental and computational data demonstrate that for $x < 0.11$, the films exhibit the face-centered cubic random solid-solution $Ni_{1-x}Al_x$ structure (γ phase). Whereas in the range x = 0.11–0.24 the γ phase coexists with the ordered L12 structure (γ′ phase). We discovered that the two phases are homogenously intermixed forming a strained coherent nanocomposite, which exhibits a single lattice parameter that expands as the Al content increases. Isothermal annealing of films containing x = 0.14 of Al, coupled with structural and nano-mechanical characterization, reveal that the coherent nanocomposite retains its overall integrity for temperatures up to 673 K, while the film hardness increases from 5.5 GPa (as deposited films) to 6 GPa. Further increase of the annealing temperature to 873 K and 1073 K causes the coherent nanocomposite to dissolve into distinct γ and γ′ phase domains and the hardness to decrease down to values of 4 GPa. These findings confirmed the metastable nature of the as-deposited thin $Ni_{1-x}Al_x$ alloy films and underpin the effectiveness of high supersaturation/undercooling for creating novel non-equilibrium phases and self-organized nanostructures upon synthesis of multicomponent materials.

Another class of crystalline multicomponent materials we investigated, are the high-entropy alloys (HEAs). Conventionally, HEAs are described as ideal solid solutions in which alloy elements are distributed randomly in the crystalline lattice (i.e., it is equiprobable to find any of the alloy elemental species on each lattice site). Concurrently, pair-wise bond strength is element specific, thereby providing a driving force that counteracts the high configurational entropy] of the lattice and may cause deviation from randomness by formation of specific clustering patterns at the nanoscale (SRO). Numerous computational studies have predicted the existence of SRO and postulated that it is important for the structure formation and mechanical properties of HEAs. However, direct experimental observation, quantification, and control of SRO via materials processing remain controversial topics. We contributed towards addressing the above-mentioned challenges by studying phase formation and nanoscale structure within the bcc W-Ta-Nb-V-Mo refractory HEA. We elected to synthesize the alloys in the form of thin films using vapor-based atom-by-atom deposition (magnetron sputtering). This far-from-equilibrium synthesis approach provides facile access to metastable structures and atomic configurations, which we sought to explore. Moreover, in thin-film synthesis methods control of alloy composition, including unintentional incorporation of impurity species, is superior to that of bulk synthesis. We combined synthesis, advanced nanoscale characterization (using atom probe tomography) and molecular dynamics simulations and found clear evidence of quasi-periodic clustering of Nb atoms the magnitude of which changes as a function of synthesis temperature. This study is the first step toward quantifying and controlling SRO in compositionally complex alloys.

Besides crystalline materials, we also turned our attention towards metallic glasses, an important glass of structural alloys with unique properties and functionalities. Identifying alloy compositions suitable for metallic glass formation from the vast and multidimensional space of elemental combinations remains a significant challenge. We developed—using literature data—a Bayesian machine learning model based on Gaussian process classification for predicting the glass forming ability (GFA) of metal-alloy compositions. The model incorporates a wide variety of descriptors computed based on the alloy compositions and physical properties of the constituent elements. With the optimal descriptor set the model achieved a prediction accuracy of 87% on an independent test set. We then applied the model to the archetypal Cu-Zr-Al ternary metallic glass system, while we experimentally synthesized thin alloy

films of selected compositions using magnetron sputtering. By characterizing the as-deposited sample structures and their evolution under heat treatment, we verified that the model captures the composition-GFA relationships well. The overall results presented herein show that our model can provide valuable guidance for the design of a wide range of amorphous alloys.

We also contributed, we advanced ion-beam analyses methods to the composition determination in alloy films synthesized by our collaborators at Linköping University with the purpose of: (i) evaluating the reliability of Vegard's rule for determining composition in Ti-Al-N coatings; and (ii) assessing the relevance of novel chemical pathways for synthesizing Ga2O3 films.

The results of our investigations led to the following publications:

Article 4
Z. Chen, A.J. J. Fellman, K. Mulewska, K. Mizohata, D. Gambino, Y. Ge, E. Lu, F. Djurabekova, A. Delimitis, L. Kurpaska, F. Tuomisto, and **K. Sarakinos**, "Formation of coherent nanocomposite structure in nickel-aluminum alloys synthesized far from equilibrium", Acta Mater. 302 (2026) 121674. (https://doi.org/10.1016/j.actamat.2025.121674)

Article 5
P. Mpofu, T. Larsson, O. Alm, J. Lauridsen, K. Mizohata, B. Spencer, H. Högberg, K. Sarakinos, and H. Pedersen, "On the reliability of Vegard's law in compositional analysis of chemical vapor deposited AlxTi1-xN", Surf. Coat. Technol. 518 (2025) 1322898. (https://doi.org/10.1016/j.surfcoat.2025.132898)

Article 6
P.S. Mushore, P. Mpofu, K. Mizohata, **K. Sarakinos**, N. O'Brien, and H. Pedersen, "Atomic Layer Deposition of Gallium Oxide using Gallium Triazenide and Water", under review in J. Phys. Chem. C (2025).

Article 7
Xuliang Luo, Tero Mäkinen, Wenyi Huo, Silvia Bonfanti, Zhehao Chen, Kenichiro Mizohata, **Kostas Sarakinos**, and Mikko Alava, "Data-Driven Prediction of Thin-Film Metallic Glass Forming Ability via Bayesian Classification and Experimental Verification in the Cu-Zr-Al System", under review on J. Appl. Phys. (2025).

Article 8
Spyridon Korkos, Zhehao Chen, Marcus Hans, Milad Ghaemi, Kenichiro Mizohata, Andreas Delimitis, Flyura Djurabekova, Filip Tuomisto, Jochen M. Schneider, and Kostas Sarakinos, "Phase formation and nanoscale structure in magnetron-sputtered W-Nb-V films", manuscript in final preparation (2025).

Fabrication of metal-graphene heterostructures

Graphene is a 2D material with a unique electronic structure, due to its linear dispersion relation and zero bandgap. This electronic structure, along with graphene's atomically thin (2D) nature and exceptional mechanical properties allows the fabrication of extremely compact and efficient devices, thus meeting ongoing miniaturization demands within the semiconductor industry, while opening new opportunities in flexible displays and stretchable sensors. Graphene can be functionalized by chemical modification of its surface or by interfacing it with other materials, thus forming heterostructures. This versatility enables tuning of its electronic and optical properties for specific applications. Graphene-based devices require fabrication of multifunctional contacts in the form of metallic layers on the graphene substrate. These layers are commonly deposited using vapor condensation techniques including thermal and electron beam evaporation. In addition to these vapor-based methods, wet-chemistry techniques and electroless deposition have been utilized to coat graphene surfaces with metal films. However, these approaches face challenges in achieving uniform film thickness and consistent material properties across large areas. Moreover, they lack precise control over the atomic-scale growth kinetics, which is essential for tailoring metal-layer morphologies and optimizing the film/substrate interface properties. Magnetron sputtering, a vapor-phase deposition method, addresses aforementioned limitations by enabling uniform thin-film deposition over large areas, while providing extensive control over process parameters to influence growth kinetics and film morphology. Concurrently, the sputtering process is associated with energetic neutral and ionized species, which can induce defects in graphene, and degrade its pristine electronic and transport properties. We systematically study the effect of hyperthermal species—an inherent feature of magnetron sputtering discharges—on the structure of single-layer graphene (SLG) upon deposition of thin metal films. Our focus is sputtered particles and backscattered process gas (argon - Ar) atoms, both generated at the sputtering target and transported through the gas phase to the substrate. We deposit 2

nm thick gold (Au), silver (Ag), copper (Cu), and aluminium (Al) layers on SLG supported on silicon dioxide substrates. We combined experiments and atomistic simulations and found that defects in SLG for all sputtered metals studied are primarily generated by energetic backscattered particles. Hence, accurate and careful control of the energy and flux of backscattered process gas atoms may allow for defect-free deposition of metal layers on graphene and thereby enable magnetron sputtering for scalable fabrication of multifunctional metal contacts in 2D-materials-based heterostructure devices.

This study led to the following manuscript:

Article 9
Franck L. Nadji Adjim, Nikolaos Pliatsikas, Olga Karabinaki, Fredric Granberg, John Arvanitidis , Dimitrios Christofilos, and **Kostas Sarakinos**, "Unravelling the effect of hyperthermal species on defect generation in single-layer graphene upon sputter deposition of thin metal films", manuscript in final preparation (2025).

Device fabrication

Using the knowledge generated by our fundamental studies of metal film growth on weakly-interacting substrates, we explored the viability of our growth manipulation strategies for fabricating thin-film based devices.

In a first study, we investigated the interface properties of gold (Au) decorated graphenized surfaces of 4H-SiC intended for electrochemical electrodes. These were fabricated using a two-step process: discontinuous Au layers with a nominal thickness of 2 nm are sputter-deposited onto 4H-SiC substrates with different graphenization extent—zero-layer graphene (ZLG) and monolayer epitaxial graphene) —followed by thermal annealing. By performing combined morphometric analysis, Raman mapping analysis, conductive atomic force microscopy, and electrochemical impedance spectroscopy measurements, we shed light on the relationship between physical processes (Au intercalation, particle re-shaping, and de-wetting) caused by thermal annealing and the intrinsic properties of graphenized SiC (vertical electron transport, charge-transfer properties, vibrational properties, and catalytic activity). We found that the impedance spectra of all considered structures exhibit two semicircles in the high and low frequency regions, which may be attributed to the graphene/ZLG/SiC (or Au/graphene/ZLG/SiC) and SiC/ZLG/graphene/electrolyte (or SiC/ZLG//Au/electrolyte) interfaces, respectively. An equivalent circuit model was proposed to estimate the interface carrier transfer parameters. This work provided an in-depth comprehension of the way by which the Au/2D carbon/SiC interaction strength influences the interface properties of heterostructures, which can be helpful for developing high performance catalytic and sensing devices.

In a second study, we deployed transparent conducting Ag layers as electrodes for replacing indium tin oxide in silicon heterojunction solar cells. Silicon heterojunction (SHJ) solar cells combine high efficiency with low-temperature processing, but high indium consumption in the transparent conductive material and silver usage in the metal grid remain key cost limitations. We demonstrated indium-free, metal-grid-free SHJ cells using a nanometer-scale thin Ag layer capped with ZnO:Al as transparent conductive material. Prototype cells and modules were fabricated by depositing Ag/ZnO:Al stacks on 2.4 × 4.8 cm2 silicon heterojunction precursors on both n- and p-sides, yielding an open circuit voltage of 690 mV after annealing. The short circuit current is limited to 31 mA/cm2 by the reflection of the Ag layer and unoptimized ZnO:Al thickness, but simulations predict that values beyond 38 mA/cm² can be achieved. Solder coated copper wires provide a low contact resistivity of 37 mΩ/cm2 to the stacks, which is two orders of magnitude lower than that achieved for ITO (3.2 Ω/cm2). Mini modules exhibited fill factors of 66%, limited by small sample size and possible Schottky contacts at either the p-type or n-type a-Si layer. Raytracing simulations indicate current generation comparable to conventional ITO/metal-grid SHJ cells when reducing the Ag layer thickness. Finite difference simulations predict fill factors above 80% with fewer than 25 wires per M2 cell, confirming the potential of thin Ag/ZnO:Al stacks as the transparent conductive material for low-cost SHJ modules.

The results of this part of the project resulted in the following publications:

Article 10
Ivan Shtepliuk, Jing-Xin Jian, Nikolaos Pliatsikas, Emanuela Schiliro, Tihomir Iakimov, Gholamreza Yazdi, Ivan G. Ivanov, Filippo Giannazzo, **Kostas Sarakinos**, and Rositsa Yakimova, "Electrochemical performance of gold-decorated graphene electrodes integrated with S", Microelectronic Engineering 278 (2023) 112042. (https://doi.org/10.1016/j.mee.2023.112042)

Article 11
M. Brinkmann, F. Haase, R. Gunnarsson, V. Elofson, **K. Sarakinos**, H.-P. Sperlich, H. Nonnenmacher, A. Waltinger, and H. Schulte-, "Thin silver layers for metal grid free and indium-free silicon heterojunction solar cells, under review in for Solar Energy Materials and Solar Cells (2025).

Simulations and model development

Along with our experimental studies, we performed theoretical investigations pertaining growth and multiscale morphological evolution of thin film and we have been developing a machine learning augmented model for simulating growth of multicomponent thin film materials.

We modelled the temperature-dependent (500 - 1300 K) diffusion dynamics of Ag, Au, and Cu adatoms on MoS2 as well as electronic and magnetic properties of adatom (Ag, Au, and Cu)/MoS2 systems. Modeling was done by means of ab initio molecular dynamics (AIMD) simulations that account for van der Waals corrections and electronic spin degrees of freedom in the framework of density functional theory. It was found that Ag and Au adatoms exhibit super-diffusive motion on MoS2 at all temperatures, while Cu adatoms follow a random walk pattern of uncorrelated surface jumps. The observed behavior is consistent with AIMD-calculated effective migration barriers Ea and can be understood on the basis of the considerably flatter potential energy landscapes encountered by Ag and Au adatoms on the MoS2 surface (corrugation of the order of tens of meV), as compared to Cu adatoms (corrugation of the order of 100meV). Moreover, evaluation of the electronic and magnetic properties of AIMD configurations suggested that Ag, Au, and Cu monomer adsorption induces semimetallic features in at least one spin channel of the adatom/MoS2 electronic structure at elevated temperatures. The overall results of this study may provide insights into fabricating 2D-material-based heterostructure devices beyond graphene.

We also performed molecular dynamics simulations to understand the morphology of film deposited on superconductive cavities. The use of superconducting radio frequency (rf) cavities in particle accelerators necessitates that copper (Cu) surfaces are coated by thin niobium (Nb) films, predominantly synthesized by magnetron sputtering. A key feature of the rf cavities is that they exhibit a complex three-dimensional geometry, such that during Nb film growth vapor is not deposited on a flat substrate. The latter, combined with the line-of-sight nature of the deposition flux in conventional magnetron sputtering methods (including direct current magnetron sputtering; DCMS) yields films with porous columnar morphologies on surfaces of the cavities that do not face the magnetron source. High-power impulse magnetron sputtering (HiPIMS) is a variant of sputtering that generates highly-ionized fluxes. Using electrical fields, such fluxes can be deflected to trajectories that are closer to the substrate normal and, thereby, dense and uniform layers can be deposited on all surfaces of therf cavities. We use classical molecular dynamics simulations to model Nb film growth on Cu substrates at conditions consistent with those prevailing during DCMS and HiPIMS. Our computational results were in qualitative agreement with experimental data (also generated in the present study), with respect to film morphology. Based on this agreement and by studying the evolution of the simulated systems, we suggested that the morphology of HiPIMS-grown films (as compared to their DCMS counterparts) is the result of the combined effects of deflection of ionized sputtered particles to trajectories parallel to the substrate normal, bombardment-induced interruption of crystal growth, and ballistic atomic rearrangement along with dynamic thermal annealing caused by energetic film-forming species. Moreover, the predictions of our model with respect to dynamic processes at the film-substrate interface and their effect on local epitaxial growth were discussed. The overall conclusion of that study is that knowledge-based design of plasma coating processes for the Nb-Cu system for the next generation of rf cavities can be supported by strategically combining atomistic simulation with characterization tools capable of providing structural and compositional information at the nanoscale.

In parallel with the computational studies, we have been developing a novel, machine-learning augmented kinetic Monte Carlo (ML-KMC) tool for modeling deposition, diffusion, and growth of metal films on fcc surfaces. The model overcomes the challenges pertaining to intermediate energy minima along the migration paths and overhang positions by allowing hops to multiple distances, i.e., landing in those intermediate minima or diffusion over stepedges. Lattice sites for new facets at arbitrary angles and hcp stacking faults are freely generated as necessary.

The atomic diffusion rates are learned on-the-fly, yielding an efficient and accurate description of kinetics without requiring any a priori knowledge of the likely diffusion events or any particular sampling scheme of the training data. We have demonstrated the feasibility of our by simulating Ag homoepitaxy on (111) surface and found that the model correctly captures island nucleation density and shape evolution at different temperatures. Concurrently, the model can be readily extended to multiple chemical elements and hence can be viewed as the first crucial step towards fast and accurate modeling of surface dynamics of multicomponent thin films on chemically heterogeneous substrates.

The theoretical studies resulting in the following publications

Article 12
M. Ghaemi, A. Lopez-Cazalilla, **K. Sarakinos**, G.J. Rosaz, C.P. Carlos, S. Leith, S. Calatroni, M. Himmerlich, and F. Djurabekova, "Growth of Nb films on Cu superconducting radio frequency cavities by direct current and high power impulse magnetron sputtering: an molecular dynamics and experimental study", Surf. Coat. Technol. 476 (2024) 130199. (https://doi.org/10.1016/j.surfcoat.2023.130199)

Article 13
M. Zarshenas, D.G. Sangiovanni, and **K. Sarakinos**, "Diffusion and magnetization of metal adatoms on single-layer molybdenum disulfide at elevated temperatures", J. Vac. Sci. Technol. A 42 (2024) 023409. (https://doi.org/10.1116/6.0003207)

Article 14
J. Kimari, F. Djurabekova, and **K. Sarakinos**, "Modeling thin-film growth by machine-learning-augmented kinetic Monte-Carlo", manuscript in final preparation (2025).