

New Horizons in Coatings and Thin Films

Room On Demand - Session F1

Nanomaterials and Nanofabrication

F1-1 Theory and Applications of Inverted Fireballs, Gerhard Eichenhofer (eichenhofer@4a-plasma.eu), 4A-PLASMA, Germany; J. Gruenwald, G-Labs, Austria

Inverted Fireballs have been proven to be a viable tool for large area surface modifications, especially for coating purposes [1, 2]. This novel technology enables energy efficient deposition for various fields of applications. Its suitability for surface modifications in general and for deposition technologies in particular is owed to their very homogeneous plasma potential and their enhanced ion densities. It has been shown that a substantial increase in the degree of ionisation in the deposition plasma is feasible. This work will outline theoretical investigations into inverted fireballs, such as analytical models and particle-in-cell simulations [3-5] and the application of these findings to technologically relevant topics. Details of how these plasma phenomena can be utilised in possible areas of surface technology, will be shown. Furthermore, it will be demonstrated that inverted FBs exhibit a number of plasma instabilities. However, they can be stabilised over a long period of time, which is necessary for industrial applications. It will also be outlined in this talk where the limitations of fireball research are at the moment and some ideas for future work on pulsed inverted FB deposition will be presented.

F1-2 Pulsed Aerosol Assisted Plasma Deposition: Influence of the Injection Parameters on ZnO/DLC Nanocomposite Thin Films, Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr), LAPLACE, LCC, France; G. Carnide, LAPLACE, LCC, IMRCP, France; A. Mingotaud, IMRCP, France; M. CAVARROC, Safran Tech, France; M. Kahn, LCC, France; R. Clergereaux, LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous [1, 2] or nanocomposite [3, 4, 5, 6]. For example, the nebulization of colloidal solutions, *i.e.* liquid solutions containing nanoparticles, in different plasma processes has been widely used for nanocomposite thin film deposition. However, nanoparticles loaded droplets in the aerosol lead to the deposition of aggregated nanoparticles embedded in the matrix.

Recently, a new process of nanoparticles injection has been developed [7]. This method, called reactor-injector of nanoparticles, consists in synthesizing nanoparticles prior to their injection in the plasma in a pulsed injection regime. It enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in the matrix [7].

This work aims to study the deposition of ZnO/DLC nanocomposite thin films in a low-pressure RF plasma. The main challenge of this process is to find the best compromise between the parameters for an efficient synthesis of ZnO nanoparticles and an optimal behaviour of low-pressure RF plasmas in a pulsed regime. It is shown that the operating window enables to deposit nanocomposite thin films with an extended range of volume fraction.

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F1-3 Design of Functional Nanoporous Ceramic Coatings via Infiltration of Polymer Templates, Diana Berman (diana.berman@unt.edu), University of North Texas, USA

Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis (SIS) with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal SIS, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the SIS material selection restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the SIS process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-assisted SIS. Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the SIS can be extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

F1-4 Improvement of Adhesion between NiTi Alloy and Diamond-like Carbon Film by Bayesian Optimization, Masafumi Toyonaga (m.tyng.keio@gmail.com), Keio University, Japan; T. Hasebe, Keio University, Tokai University Hachioji Hospital, Japan; S. Maegawa, Tokai University Hachioji Hospital, Japan; T. Matsumoto, Keio University, Tokai University Hachioji Hospital, Japan; A. Hotta, T. Suzuki, Keio University, Japan

Surface coating is one of the most interesting methods for improving the mechanical, physical, chemical and biocompatible properties of materials and devices. Fluorine-incorporated diamond-like carbon (F-DLC) has received much attention as a coating material because of outstanding blood compatible properties which suppress fatal failure of the medical devices. However, it is well known that F-DLC thin films exhibit poor adhesion on metallic alloys and delamination or cracks are easy to occur after coating. In order to improve adhesion of F-DLC on metallic alloys, many scientific methods have been reported. Although some of these studies focused on introducing silicon-containing interlayers such as silicon-incorporated DLC (Si-DLC) between metallic alloys and F-DLC thin films to improve the adhesion properties, the film formation conditions of the interlayer that most improves the adhesion are not clear, and the method has not been established for optimizing the film formation conditions. Thus, we considered optimizing the structure of the interlayer using "Bayesian optimization", which is known as one of machine learning. In this study, we optimize the structure of Si-DLC interlayer by Bayesian optimization to apply F-DLC to low blood compatible nickel-titanium (NiTi)

alloy, which has been attracting attention as a material for medical devices due to superelasticity and shape memory.

The purpose of this study is evaluating the effectiveness of Bayesian optimization for determining optimal structures of interlayers between metallic substrates and F-DLC, and developing high blood compatible NiTi alloy by improving adhesion properties of F-DLC.

Si-DLC and F-DLC were prepared on NiTi substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) equipment. The adhesion properties between NiTi substrates and DLC thin films were evaluated by the scratch test, and the structures of Si-DLC interlayer were updated successively by Bayesian optimization on the obtained data. Total of 30 Si-DLC interlayers were produced, and the highest adhesion could be improved to about 53 mN, while the lowest adhesion was about 22 mN. The one with the highest and lowest adhesion were deposited on the NiTi stents, and after performing the crimp test and the fatigue test, the surface was observed by Scanning Electron Microscope (SEM). As a result, no delamination was observed in the interlayer derived by Bayesian optimization, whereas delamination occurred in the sample in which structure was not optimized.

Therefore, this study shows that adhesion properties between metallic material and DLC thin film can be improved by Bayesian optimization.

F1-5 Novel Type of Bent-Lattice Nanostructure in Crystallizing Amorphous Films Revealed by TEM: From Transrotational Microcrystals to Strain Nanoengineering and Novel Amorphous Models, Vladimir Kolosov (kolosov@urfu.ru), Ural Federal University, Russian Federation

Exotic thin crystals with unexpected **transrotational nanostructures** [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, metals) prepared primarily by vacuum evaporation methods. We use TEM bend-contour method [2] combined with selected area electron diffraction. HREM, AFM and optical microinterferometry were used in due cases (preferentially for correlative microscopy).

The unusual phenomenon often can be observed *in situ* in TEM column during local e-beam heating or annealing: regular internal bending of crystal lattice planes in a growing crystal, Fig. 1 a-b. It is dislocation independent. Such **transrotation** (translation of the crystal unit cell is complicated by small **rotation** realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees/ μm) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc., Fig. 1b

The possible mechanisms of the phenomenon are discussed, Fig. 1d. Initial amorphous state and surface nucleation of the crystal growth are most essential factors. The last fact accompanied by anisotropy of crystal growth rate and obvious tendency for regular change of interatomic distances of the crystal propagating from the surface layers inside the bulk material resembles specific epitaxy, “vacuum epitaxy”. The transrotation phenomenon is the basis for novel lattice-rotation nanoengineering of functional, smart thin-film materials appropriate also for strain nanoengineering. Transrotational micro crystals have been eventually recognized by different authors in some thin film materials vital in applications, e.g. phase change materials (PCM) for memory [3-5].

New nanocrystalline “curved-lattice” concept for amorphous state is proposed: fine-grained structures with lattice curvature, Fig. 1e. Thus the great variety of different possible curved/transrotational lattice geometries inside fine crystal grains in the static model corresponds to different amorphous structures hardly distinguished by known methods. Going to 3D clusters of positive/negative curvature and dynamics we propose the hypothesis of “dilatons”, “contractons” pulsating or/and circulating in amorphous film.

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F1-6 Deposition of Cu and Pt Metallic Clusters onto Titanium Dioxide Nanoparticles by DC Magnetron Sputtering for Hydrogen Production, Glen West (g.west@mmu.ac.uk), Manchester Metropolitan University, UK; M. Bernareggi, G. Chiarello, E. Selli, University of Milan, Italy; A. Ferretti, ISTM-CNR Lab Nanotechnology, Italy; M. Ratova, P. Kelly, Manchester Metropolitan University, UK

A novel technique using pulsed-DC magnetron sputtering has been employed to deposit metal nanoclusters directly onto titanium dioxide nano-particles. Deposition conditions and plasma compositions were varied to produce the desired Cu and/or Pt clusters on the particle surfaces. The nanoparticle powder was placed within an oscillating substrate holder, and a top-down sputter deposition arrangement allowed deposition onto the continuously rotating nanoparticles. HRTEM analyses revealed the presence of well-dispersed, sub-nanometric sized metal clusters, even following extended deposition times, while XRD analysis showed no modification of the TiO₂ crystal structure resulting from the process.

The coated powders were then tested for their ability to produce hydrogen from a methanol photo-steam reforming process via photocatalytic action. The photo-activity of the powders was increased by the presence of Pt clusters with respect to that of bare TiO₂. During Cu sputtering, the plasma composition was found to strongly affect the photoactivity of the materials produced. Copper when deposited as a lone co-catalyst in an Ar-only atmosphere imparted better photo-activity than Cu sputtered in Ar/O₂. When the deposition process coupled both Cu clusters and Pt clusters, an additive effect of the two metals in increasing TiO₂ photoactivity for hydrogen generation was observed under optimised conditions.

F1-7 Manipulation of Thin Films and Nanostructures on Weakly-interacting Substrates by Selective Surfactant Deployment, A. Jamnig, Linköping University, IFM, Nanoscale Engineering Division, Sweden; N. Pliatsikas, M. Konpan, Linköping University, IFM, Nanoscale Engineering Division; J. Lu, Linköping University, IFM, Thin Film Physics Division, Sweden; J. Kovac, Josef Stefan Institute; G. Abadias, University of Poitiers, PPRIME Institute, CNRS, France; I. Petrov, University of Illinois, USA, Linköping University, Sweden, USA; J. Greene, University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA; Kostas Sarakinos (kostas.sarakinos@liu.se), Linköping University, Sweden

The ability to control the size and shape of noble-metal nanostructures and the morphology of noble-metal films on weakly-interacting substrates, including 2D materials and oxides, is essential for the fabrication of high-performance enabling devices. The use of less-noble-metal and gaseous surfactants is a known strategy for manipulating growth of noble-metal layers, but the mechanisms by which surfactant atoms affect the complex structure-forming processes are not yet understood. In this work, we study the effect of nitrogen (N₂) gas on the morphological evolution of magnetron-sputter-deposited silver (Ag) thin films on silicon dioxide substrates. We find that presence of N₂ in a mixed argon (Ar)/N₂ gas atmosphere, throughout all film-formation stages, promotes 2D growth and smooth film surface, while the continuous-layer electrical resistivity increases, compared to Ag films grown in pure argon (Ar) ambient. Using a combination of real-time *in situ* film growth monitoring and *ex situ* characterization, we conclude that N₂ is physisorbed on the film growth surface and promotes 2D morphology by suppressing island coalescence rates during initial growth stages. Moreover, our data suggest that physisorbed N₂ causes interruption of local epitaxial growth on Ag crystals, which leads to repeated nucleation and explains the increased electrical resistivity of continuous films. Using these insights, we deposit Ag films by deploying N₂ selectively, either during the early growth stages or after coalescence completion. We show that early N₂ deployment leads to a 2D morphology without affecting the Ag-layer resistivity, while post-coalescence introduction of N₂ in the gas atmosphere further promotes formation of 3D nanostructures and roughness at the film growth front. The knowledge generated in the present study is relevant for the development of single-step growth manipulation strategies in which gaseous and less-noble-metal surfactant species can be deployed with high temporal and spatial precision to selectively target and modify the rates of key structure-forming processes.

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