New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F1-TuM

Nanomaterials and Nanofabrication

Moderators: Ulf Helmersson, Linköping University, **Vitezslav Stranak**, University of South Bohemia

8:00am **F1-TuM-1 Single and Multi-component Nanomaterials Prepared by Means of Cluster Beam Deposition**, ***Ondrej Kylian***, Charles University, Czech Republic; *A Shelemin, D Nikitin,* Charles University, Czech Republic, Czechia; *P Pleskunov, J Hanus, P Solar, A Choukourov, A Kuzminova, M Cieslar, H Biederman,* Charles University, Czech Republic **INVITED**

Cluster beam deposition by means of gas aggregation sources (GAS) based either on magnetron sputtering or plasma polymerization become very attractive tool for the production of metal, metal-oxide or plasma polymer nanoparticles (NPs). The increasing popularity of GAS systems is caused by many advantageous features that these sources offer such as their relative simplicity, high efficiency, no or only limited use of potentially harmful solvents and precursors, cleanness of produced NPs as well as the possibility to combine gas aggregation sources with another vacuum-based deposition methods that in turn enables production of functional nanocomposite or nanostructured materials. Furthermore, recent studies showed that not only single material NPs, but also more complex multi-component NPs may be produced by GAS systems including dumbbell-like, janus-like or core@shell nanoparticles.

In this study we introduce and compare three different strategies that allow producing multi-component heterogeneous metal/plasma polymer NPs. The first one is based on the use of a composite metal/polymer target. An example of this approach is the use of Cu/nylon target mounted onto a planar magnetron introduced into the aggregation chamber of GAS. As it was found this system makes it possible to produce metal/plasma polymer nanoparticles with multiple small metallic cores embedded in a plasma polymer shell. Similar multi-core@shell structure of created NPs was observed also when the second approach was used, in which a high amount of precursor (HMDSO) was introduced into the aggregation chamber of the GAS equipped with planar magnetron used for metal sputtering (Ag in our case). The formation of multi-core@shell NPs in both of these arrangements may be explained by the competitive growth of metal NPs and plasma polymerization process and phase segregation of metals and polymers caused by the differences between the cohesive forces of metal atoms and interaction energies of metals and organics. In order to achieve single-core@shell NPs, the third strategy was developed. This is based on the in-flight coating of metallic NPs by a thin plasma polymer shell. This is realized by an auxiliary plasma deposition source positioned in between the output orifice of the GAS and substrate. It is shown that this approach enables to fully decouple the core production from the shell deposition and it is suitable for effective production of metal/plasma polymer single-core@shell NPs.

Acknowledgments: This work was supported by the grant GACR 17-22016S from the Czech Science Foundation

8:40am **F1-TuM-3 Preparation of High Activity and Stability of Cobalt Carbide Nanoparticles for Hydrogen Evolution Reaction**, ***Yi-Heng Lin***, National Cheng Kung University, Taiwan; *S Wang,* Southern Taiwan University of Science and Technology, Taiwan; *J Huang,* National Cheng Kung University, Taiwan

Hydrogen is one of the promising renewable energy in substitution for petroleum energy. The hydrogen produced by splitting water using renewable energy is the key to becoming a sustainable and environmentally friendly green energy. The catalyst plays an important role in hydrogen evolution reaction (HER) to enhance the efficiency. Among the transition metal carbides (TMCs), cobalt carbide is considered to be a potentially active catalyst from theoretical calculations and literature reports. However, the common syntheses are solid phase or chemical vapor deposition processed at high temperature. Here we report two wet-chemistry synthesis methods to prepare nano-sized transition metal carbide. For the first process, $Co(CHOCOO)_2$ and triethylene glycol (TEG) are used as cobalt and carbon source precursor, respectively. With increasing temperature and time of the reaction, TEG decomposes and Co^2+ becomes carbonized. By controlling the amount of NaOH addition, we can adjust the ratio of Co_2C and Co_3C in the product. In the other process we use TEG and oleylamine (OLA) as precursor and without participation of NaOH, and the product will be only Co_2C. The X-ray diffraction pattern peaks show that there is the presence of Co_3C in the former process, and Co_2C dominate in the latter process. The detailed analysis of the product such as TEM, SEM, FT-IR and electrochemical properties on HER will be reported in future.

9:00am **F1-TuM-4 Nanocluster-Based Metal Oxide Films for Hydrogen Gas Sensing**, ***Stanislav Haviar***, *J Čapek, Š Batková, N Kumar,* University of West Bohemia, Czech Republic

Advances in the field of hydrogen-based technologies bring new challenges for material researchers working in the field of gas sensors.

Metal oxide semiconductors (MOSs) are well established as active materials in gas sensor assemblies. Especially nanostructured MOSs attract the attention because of the unique electronic properties of nanomaterials and a high reactive area. Here, we present the study of nanostructured MOS films prepared by use of a gas aggregation cluster source (GAS).

To assemble a functional hydrogen gas sensor we combined sputter-deposited thin film of tungsten oxide with cupric oxide nanoclusters prepared by GAS. Sputtering conditions were tuned to vary the chemical composition and structure of the prepared films. Various architectures were examined for their sensorial response when assembled into a hydrogen gas sensor. The specimens were tested for the response to a time-varied hydrogen concentration in synthetic air at various temperatures. The sensitivity and the response time were evaluated. It is shown that optimization of the structure, architecture and/or composition results in enhanced sensorial properties.

The prepared materials were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy. The chemical composition was studied using X-Ray Photoemission Spectrometry (XPS) and Near Ambient Pressure XPS (NAP).

With further expansion of mobile and portable hydrogen-based technologies the demand on miniaturization of gas sensor rises. That is why it is of a key importance that both the magnetron sputtering and deposition of clusters are techniques compatible with industrial microcircuit technologies. Moreover, in contrary to commonly used wet-techniques the GAS process provides nanoparticles which are clean and ready to use for catalytic purposes in the “as-deposited” condition.

Therefore the technique is very attractive for the research of new catalytic materials.

9:20am **F1-TuM-5 Depostion of Magnetic Thin Films by High Power Impulse Magnetron Sputtering**, ***Jon Tomas Gudmundsson***, *H Hajihoseini, M Kateb, S Ingvarsson,* University of Iceland, Iceland

We study the microstructure and magnetic properties of Ni and $Ni_{80}Fe_{20}$ thin films grown by high power impulse magnetron sputtering (HiPIMS), and compare with films grown by dc magnetron sputtering (dcMS). The nickel films were grown under tilt angles ranging from 0 (substrate faces to the target) to 70 degrees. The magnetic hysteresis was characterized using a home-made high sensitivity magneto-optical Kerr effect (MOKE) looper. It is shown that both deposition methods exhibit in-plane biaxial anisotropy when deposited at small tilt angles while larger tilt angles result in uniaxial anisotropy. However, the angle of transition for anisotropy type is different when depositing with dcMS (35 degrees) compared to HiPIMS deposition (60 degrees). The $Ni_{80}Fe_{20}$ films were grown under a tilt angle of 35 degrees to identical thickness of 37 nm using both dcMS and HiPIMS [1]. All the films exhibit effective in-plane uniaxial anisotropy with square easy axis and linear hard axis magnetization traces. X-ray diffraction reveals that there is very little change in grain size within the pressure and temperature ranges explored. However, variations in film density, obtained by x-ray reflectivity measurements, with pressure have a significant effect on magnetic properties such as anisotropy field (Hk) and coercivity (Hc). We find that HiPIMS deposition results in dense films with low H_k and H_c. For epitaxial growth of $Ni_{80}Fe_{20}$ film on MgO (001) we find the film deposited with HiPIMS has very well defined in-plane uniaxial anisotropy along the <100> direction while the dcMS deposited film presents biaxial anisotropy in-plane, the easy directions are along the [110], indicating that crystalline anisotropy is dominant in that case.

[1] Kateb et al., J. Phys. D: Appl. Phys. 51 (2018) 285005

9:40am **F1-TuM-6 Fluorination of the Magnesium Particle Surface: Enhancing the Reactivity of Magnesium**, *M Pantoya,* ***Shancita Islam***, Texas Tech University, USA

Most metal fuel particles are inherently passivated with their native metal oxide to prevent the pyrophoric metal core from spontaneous reaction with the surrounding environment. The metal oxide is typically a heat sink

and barrier to diffusion limited oxidation reactions. One strategy for increasing the energy release rate of nanoparticle fuels is to activate surface reactions that promote faster and more complete main oxidation reactions. Recent work with aluminum (Al) nanoparticles has shown that the native oxide shell can be used to exothermically contribute to the overall energy generated. The goal of this study was to assess reactivity spurred from surface exothermic reactions to other fuels, namely magnesium, Mg. The objective was to examine surface reactions of Mg particles including nano and micron scale particles coated with a liquid fluorinated perfluoro-polyether (PFPE) polymer. To closely observe the properties of the exothermic surface reaction, magnesium-oxide (MgO) nanoparticles were also examined. Many experimental techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) are used to characterize the Mg-PFPE and MgO-PFPE reactions. The results showed that all samples generate a pre-ignition reaction (PIR) including micron Mg particles, and the PIR enthalpy increases with decreasing particle size. The XRD results confirm MgF_2 in all product samples. Further, activation of surface exothermic reactions was shown to affect the overall reactivity of Mg particles by combining the Mg-PFPE coated particles with another solid oxidizer, polytetrafluoroethylene (PTFE) and measuring the flame speed compared with uncoated Mg particles. Results from this study extend previous work promoting surface reactions on Al to other fuels that also benefit from this strategy.

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