

# Tuesday Afternoon Poster Sessions

## Advanced Surface Engineering

Room: Southwest Exhibit Hall - Session SE-TuP

### Advanced Surface Engineering Poster Session

**SE-TuP1 Effect of NiCr-based Bondcoat and Post Treatment Process on the Adhesion of Air Plasma Sprayed WC-Co Coatings, F. Ghadami, University of Tehran, Iran, S. Ghadami, University of Semnan, Iran**

In this study WC-12wt%Co and NiCr-based powders were sprayed by the Air Plasma Spray (APS) method to form conventional WC-Co and double-layer NiCr-based/WC-Co coatings on steel substrates. The microstructure of as-sprayed samples with and without NiCr-based bondcoat were analyzed and found WC, W<sub>2</sub>C carbides and an amorphous phases. The single layer WC-Co coating samples were also heat-treated at 650, 900 and 1150°C for 1 hr. Heat treatment at all temperatures examined resulted in phase changes within the coating layer by formation of W<sub>x</sub>Co<sub>y</sub>C, η-carbides. Adhesive strength as well as microhardness of the as-sprayed and heat-treated coatings were also investigated. Results indicated that, adhesive strength has improved by using NiCr-based bondcoat in WC-Co deposits. The results also showed that heat treatment at 900 and 1150°C improves adhesive strength and hardness in conventional WC-Co coating samples. In this case, heat treatment process at 900°C gave the highest adhesive strength among the WC-Co coatings, which was due to the formation of η-carbides in interface of coating and substrate and formation of chemical bonding.

**SE-TuP2 Nanostructured Surfaces for Electrodes Prepared by Glancing Angle Deposition, U.B. Jensen, E. Ferapontova, D.S. Sutherland, Aarhus University, Denmark**

There are many potential applications for nanostructured surfaces. The aim of this work is making better electrodes for use in bio sensors and biofuel cells. One possible application is implantable medical devices, which could be a valuable tool for diagnosis and treatment of certain diseases, e.g. diabetes. If a biofuel cell could be made to deliver enough power, the signal from a bio sensor could be transmitted wirelessly to a computer capable of analysing and acting in response to the data. [1] Furthermore, if a bio sensor was functional and accurate for long times, an implantable medical device could work for months or longer.

The present approach to this challenge is to develop nanostructured surfaces on electrodes, onto which enzymes can be attached. Since the enzymes catalyze specific reactions, this can be used for sensing of a particular bio molecule. The proposition is that by changing the nanostructures one can improve and/or tailor electrodes for any bio sensing application.

The nanostructured surfaces were prepared by a combination of two techniques: colloidal lithography and glancing angle deposition [2]. This combination allows for control of critical parameters such as porosity, curvature and shape of the nanostructures. An example of nano-scale objects is shown in the figure – gold pillars protruding from a flat surface. This surface can be of almost any material, and the nano-scale objects uniformly covers large surface areas.

In terms of applications various enzymes will be immobilised on nanostructured surfaces. After changing various surface properties prior to enzyme immobilisation the efficiency of biofuel cells and bio sensors will be determined. This will make it possible to establish which properties are optimal, and it is therefore likely that better electrodes for bio sensing and fuel cells can be developed.

[1] C. Gomez, S. Shipovskov and E. E. Ferapontova, *J. Renewable Sustainable Energy* 2, 013103, (2010)

[2] K. Robbie and M. J. Brett, *J. Vac. Sci. Technol. A* 15(3), 1460–1465, (1997)

**SE-TuP3 Spatially Controlled Heat Generation by Local Plasmon Resonator, K. Namura, M. Suzuki, R. Tabuchi, K. Nakajima, K. Kimura, Kyoto University, Japan**

Heat generation from noble metal nanoparticles due to their local plasma resonance is attracting much attention because of the fast response and the flexibility to choose heating area. The conventional nanoparticle heaters are fabricated by simple lithography of Au thin films on glass or Si substrate so that they absorb only a few 10 % of the incident light even at the wavelength of the local plasma resonance. Therefore, they are ineffective from the viewpoints of not only the fabrication cost but also photothermal conversion. In addition, it is difficult to spatially control the generated heat

because photothermal conversion efficiency is constant for all nanoparticles.

Recently, we demonstrated the self-assembling of Au nanoparticles/dielectric layer/ Ag mirror sandwiches, namely, the local plasmon resonator, by using a dynamic oblique deposition technique<sup>1</sup>. Due to strong interference, their optical absorption can be controlled between 0.1% and 100% by changing the thickness of the dielectric layer. Although we focused our attention only on the local field enhancement in that work, now we notice that photothermal conversion efficiency can be spatially tuned by using the local plasmon resonators. This work is the feasibility study of application of the local plasmon resonator to the spatially controlled nanoheaters.

We prepared combinatorial local plasmon resonator chips which have different thicknesses of Au and the dielectric layers on a single substrate of 50×50 mm<sup>2</sup> by oblique deposition and measured the absorption spectrum on each element. In order to evaluate the heat generation from Au nanoparticles, we measured the temperature of the water, with which a small cell created on a local plasmon resonator was filled, irradiating the laser of the wavelength of 785 nm. The temperature of the water on the element with high absorption becomes higher than that on the element with low absorption. The change in temperature proportional to absorption of the element in the local plasmons resonator chips. This suggests that the photothermal conversion efficiency can be controlled by the interference. Consequently, local plasmon resonator can be applied to the nanoheaters, which can spatially control the heat generation.

This work was supported by KAKENHI 21656058 and by the Iketani Science Foundation.

1. M. Suzuki, *et al.*, *Journal of Nanophotonics*, **3**, 031502 (2009).

**SE-TuP4 Multifrequency Atomic Force Microscopy with Heated Cantilever Tips, J.L. Remmert, Universal Technology Corporation, J.G. Jones, A.A. Voevodin, Air Force Research Laboratory, W.P. King, University of Illinois at Urbana-Champaign**

Multifrequency drive capabilities have recently been implemented on the atomic force microscope (AFM) to enhance imaging contrast and retrieve information about the material properties of the sample surface<sup>1</sup>. Common to each technique is the use of a complex (amplitude-modulated) waveform to oscillate the cantilever tip in proximity to the substrate at two or more of its flexural resonances. Simultaneous measure of the amplitude and phase of the cantilever ac deflection is used to characterize the tip-sample coupling and may, for example, relay mechanical and chemical information through the separation of short- and long- range forces between distinct resonance modes<sup>2,3</sup>. In this way, bimodal imaging has also advanced magnetic<sup>3</sup> and electrostatic<sup>4</sup> force mapping with the application of appropriate fields. Related techniques track spatial variations in the contact resonance by evaluating the cantilever response across either a frequency band (band excitation, BE) or at fixed limits bracketing the peak (dual ac resonance tracking, DART). Resonance tracking also reduces crosstalk between the surface topography and frequency-dependent material properties, and has been employed to measure energy dissipation<sup>5</sup>, as well as for piezoelectric domain characterization<sup>6</sup> and local thermal analysis<sup>7</sup> with drive signals modulating the local electrical bias and temperature gradient, respectively. This work focuses on the latter approach: the use of dual frequency excitation to resistively heat and actuate an AFM tip for thermomechanical imaging of sample surfaces. Evaluation of the ac deflection at two frequency limits provides the amplitude and phase data required to extract the quality factor (dissipation) by the simple harmonic oscillator model<sup>1</sup>. The experimental procedure (thermal DART) has been demonstrated along with data post-processing to establish a temperature-dependent study of surface mechanical properties.

<sup>1</sup>R. Proksch and C. Callahan, United States Patent Application Publication US 2009/0013770 A1 (2009).

<sup>2</sup>R. Proksch, *Applied Physics Letters* **89**, 113121 (2006).

<sup>3</sup>J.W. Li, J.P. Cleveland, and R. Proksch, *Applied Physics Letters* **94**, 163118 (2009).

<sup>4</sup>R. W. Stark, N. Naujoks, A. Stemmer, *Nanotechnology* **18**, 065502 (2007).

<sup>5</sup>S. Jesse, S.V. Kalinin, R. Proksch, A.P. Baddorf, and B.J. Rodriguez, *Nanotechnology* **18**, 435503 (2007).

<sup>6</sup>B. J. Rodriguez, C. Callahan, S. V. Kalinin, and R. Proksch, *Nanotechnology* **18**, 475504 (2007).

<sup>7</sup>M.P. Nikiforov, S. Jesse, A.N. Morozovska, E.A. Eliseev, L.T. Germinario and S.V. Kalinin, *Nanotechnology* **20**, 395709 (2009).

**SE-TuP5 Time Domain Thermoreflectance and 3-Omega Comparison Studies of Polymer-Metallic-Ceramic Nanolaminate Coatings.** *A.R. Waite*, Air Force Research Laboratory/Universal Technology Corp., *J.J. Gengler*, Air Force Research Laboratory/Spectral Energies, LLC, *J.G. Jones*, *C. Muratore*, *A.A. Voevodin*, Air Force Research Laboratory

Multilayered polymer-metal-ceramic nanolaminate coatings were grown by room temperature plasma enhanced chemical vapor deposition (PECVD) and magnetron sputtering processes in a dual chamber PVD-CVD system to examine optical coatings with tailored, through-thickness thermal conductivity. Highly cross-linked fluoropolymer films were grown by PECVD from an octafluorocyclobutane gas precursor. High refractive index ceramic layers were deposited by pulsed DC magnetron sputtering of a TiO<sub>2</sub> target. Thin (5-20 nm) silver interlayers with thicknesses on the order of phonon mean free paths were also integrated into the nanolaminate stack. The thickness and position of the layers with high and low refractive index layers could be adjusted to develop optical coatings with desired functionality for different wavelengths of incident light, while metal layers were integrated to distribute heat and eliminate decomposition of the polymer films during heating by incident light. The through-thickness thermal conductivity of the films with and without the integrated silver layers was compared by time domain thermoreflectance (TDTR) and 3-Omega techniques. The 3-Omega analysis provides the bulk thermal conductivity of the nanolaminate stack which was compared to the constructed thermal transport model from the TDTR analysis of each film material and their respective interfaces.

**SE-TuP6 Water Adsorption on TiN and TiCN Hard Coatings.** *E. Broitman*, Carnegie Mellon University, *M. Rebelo de Figueiredo*, University of Leoben, Austria, *W. Michalak*, Carnegie Mellon University, *R. Franz*, University of Leoben, Austria, *G. Zanini Gadioli*, Carnegie Mellon University, *C. Mitterer*, University of Leoben, Austria

It is known that ceramic coatings with substantial amounts of structurally incorporated carbon show low-friction behavior, in particular at intermediate temperatures. However, the mechanisms behind activation, formation and modification of the required free carbon in the friction contact are still not fully understood, especially in the case of Ti<sub>x</sub>CN<sub>y</sub>, a widely used commercial coating. In a previous study the importance of the presence of water vapor for the formation of a friction-reducing layer has been revealed by tribological tests at different water vapor pressures in the surrounding atmosphere. In the present work, water adsorption studies on titanium nitride (TiN) and titanium carbon nitride (TiCN) coatings are carried out in order to gain a new insight about the active chemical processes on the coating surface.

The TiN and TiCN coatings were prepared by dc magnetron sputtering of a TiN and Ti<sub>2</sub>CN compound target, respectively, in a lab-scale deposition system. X-ray diffraction was used to study the crystal structure and the obtained patterns show a face-centered cubic structure with a [111] texture for TiCN and a [200] texture for TiN. Both X-ray Photoelectron Spectroscopy (XPS) and Temperature Program Desorption (TPD) experiments in the range 110-700 K were conducted in an Ultra High Vacuum chamber with a base pressure of ~ 3 x 10<sup>-10</sup> Torr. Also, the water adsorption on the coatings as a function of % relative humidity was measured using a quartz crystal microbalance.

XPS measurements reveal the presence of a surface oxide, with the composition of the coatings being Ti<sub>2.0</sub>N and Ti<sub>1.73</sub>CN<sub>1.35</sub>. TPD experiments show that water adsorption has a zero-order desorption mechanism. After low coverage and temperature of exposure of 110 K, the spectra yield calculated desorption energies of 22.96 ± 4.17 kJ/mol and 18.42 ± 4.73 kJ/mol for the TiN and TiCN surfaces, respectively, based on a leading-edge analysis. Measurements from higher coverage indicate the strength of the water-water attractive interactions which cause clustering of H<sub>2</sub>O into 2-D islands and then multilayers. The desorption energies from this regime are calculated to be 47.45 ± 2.31 kJ/mol and 41.73 ± 4.06 kJ/mol for the TiN and TiCN surfaces, respectively. These values are higher than the water's combined heats of vaporization and fusion: ΔH<sub>v</sub> + ΔH<sub>f</sub> = 9.72 kcal/mol + 1.44 kcal/mol. The water adsorption results can be correlated to the microstructure, composition and tribological properties.

**SE-TuP7 Effects of Ag/Cu Ratios on the Annealing Temperature and Mechanical Properties of TaN-(Ag,Cu) Nanocomposite Thin Films.** *J.H. Hsieh*, *S.Y. Hung*, Ming Chi University of Technology, Taiwan, Republic of China, *S.Y. Chang*, *C.C. Tseng*, National Chung Hsing University, Taiwan, Republic of China

TaN-(Ag,Cu) nanocomposite films were deposited by reactive co-sputtering on Si(110) substrates. The samples were then annealed using RTA (Rapid Thermal Annealing) at various temperature (200 °C ~ 400 °C) for 2, 4, 8 minutes respectively to induce the nucleation and growth of Ag/Cu particles in TaN matrix and on film surface. This study was attempted to find out if annealing temperature and mechanical properties

were affected by Ag/Cu ratios. C-AFM (Conductive Atomic Force Microscopy) and FESEM (Field Emission Scanning Electron Microscopy) were used to confirm the emergence of Ag/Cu nano-particles on the surface of TaN-(Ag,Cu) thin films. Nano-indenter was used to examine the mechanical properties of the films. The results reveal that annealing temperature could be as low as 200 °C for the sample with Ag/Cu ratio at 4:6, while the hardness values could be at their highest. Accordingly, the films may be applied on polymeric substrate in the future for the purpose of anti-wear and anti-bacteria.

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