Monday Morning, April 24, 2017

New Horizons in Coatings and Thin Films Room Royal Palm 1-3 - Session F1-1

Nanomaterials and Nanofabrication

Moderators: R. Mohan Sankaran, Case Western Reserve University, Sumit Agarwal, Colorado School of Mines

10:00am F1-1-1 Sculptured Thin Films by Ion Beam Sputtering, Bernd Rauschenbach, C Grüner, Leibniz Institute of Surface Modification, Germany

Nanostructures with a three dimensional tailored shapes are promising candidates for a variety of applications. The sputter induced glancing angle deposition technique is a sophisticated method to create nanostructures with custom-made structure geometries. This new technology is characterized, that the sputtered particle flow arrives the substrate under an extremely grazing angle. In the consequence highly porous thin films are produced, which consist of slanted needles. An additionally constant or periodically interrupted substrate rotation during sputter induced deposition is used to tailor structures like chevrons, posts, circular and quadratic spirals or zig-zags. The structure formation is based on geometric shadowing, where the arriving particle flux is supposed to be caught by the top of structure, and no growth occurs in the structure shadow.

In this presentation a report about the growth nanostructures on nonpattered and regularly arranged nanostructures and the growth conditions is given and some applications of such three-dimensional nanostructures are demonstrated. The growth of the nanostructures is studied in dependence on substrate temperature, substrate pre-patterning, substrate rotation speed, and deposition rate using scanning electron microscopy, Xray diffraction and high-resolution transmission electron microscopy. The metal and semiconductor nanostructures were grown using ion beam sputter induced GLAD in an ultrahigh vacuum chamber [1-4].

Because this process provides precise nanoscale control over the structure and grain orientation characteristics, the mechanical, magnetic and optical properties of the sculptured films may be engineered for various applications. Finally, recent studies on first applications will be presented [5-6].

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[5] C. Grüner, B. Rauschenbach, Appl. Phys. Lett. 95 (2009) 103107

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10:20am F1-1-2 The Effect of Thermal Treatment on the Structure and Surface Plasmon Resonance of Ag-coated ZnO Nanoparticles by Sol-gel Method, *Chih-Chiang Wang*, National Chung Hsing University, Taiwan; *H Shih*, Chinese Culture University, Taiwan

Zinc oxide (ZnO) is an n-type II-VI semiconductor with a hexagonal wurtzite structure, a wide band gap (3.3 eV) and a higher exciton binding energy (60 meV), and has been applied in the field of ultraviolet or visible optoelectronic devices, photocatalyst, gas sensors, solar cells. On the other hand, silver (Ag) nanoparticles show the variable surface plasmon resonance (SPR) properties by controlling the particles shape, size, and density. In this study, the ZnO nanoparticles were fabricated by sol-gel method at the ambient environment. Subsequent baking was conducted at the 500°C in air. The Ag nanoparticles were coated on the ZnO surface by surface decoration process and baked in the lower pressure condition (~10- 3 torr) at several temperatures (100, 300, and 500°C).

XRD patterns showed that peaks of (100), (002), (101), (102), (110), (103) planes belonged to the pure ZnO nanoparticles as the wurtzite structure. The peak of (111) plane at 38.1° appeared at the baking temperature of 300

and 500°C indicating that the Ag metal and its grain size increased with the increasing baking temperature. The TEM images and SAD patterns indicated that the Ag-coated ZnO nanoparticles kept the same crystal structure with a prominent facets (002) of the ZnO and (111) of the Ag nanoparticles.

The PL spectra displayed a tendency of blue shift in the UV light emission of 3.18 to 3.2eV and 3.08 to 3.1eV, respectively, while the Ag nanoparticles size increased. The former was the intrinsic emission, and the latter was caused by the V₀⁺. Raman spectra revealed the peaks at 99cm⁻¹ (E_2^{low}), 331cm⁻¹ (multiphonon), 439cm⁻¹ (E_2^{high}), and 580cm⁻¹ (E_1LO). The intensity of E_2^{low} mode showed the apparent increasing as the baking temperature increased. However, the intensity of multiphonon, E_2^{high} , and E_1LO mode revealed the opposite tendency. The binding energy in XPS analysis of the Zn2p_{3/2} and Zn2p_{1/2} were observed at 1021.3 and 1044.8eV, respectively. In addition, the deconvolution of Ag3d_{5/2} showed 368.5 (Ag⁰) and 367.4(Ag⁺)eV. The ratio (Ag⁰/Ag⁺) increased with the increasing baking temperature, meaning more Ag metals on the Ag-coated ZnO nanoparticles. The UV-Vis spectrum revealed the noticeable peak centered at λ =420nm due to the SPR effect of Ag nanoparticles, and showed the red shift to λ =460nm as the Ag nanoparticles size increased.

10:40am F1-1-3 In-situ Electron Microscopy of Synthesis, Chemistry and Self-Assembly of Colloidal Nanostructures, Eli Sutter, University of Nebraska-Lincoln, USA INVITED

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

11:20am F1-1-5 Deposition of PTFE – TiO₂ Composite Coatings Combining Superhydrophobic and Photocatalytic Properties by Reactive pDC Magnetron Sputtering from a Blended Powder Target, *Marina Ratova*, *P Kelly*, *G West*, Manchester Metropolitan University, UK

Photocatalytic materials are used as a sustainable approach to air and water purification, water splitting and decontamination and disinfection of surfaces. Superhydrophilicity (water contact angles of 10° or lower) is one of the widely reported features of titania-based photocatalytic surfaces. However, superhydrophobic surfaces (water contact angles of 150° or higher) are often more desirable for environmental cleaning than superhydrophilic ones, as they prevent adhesion of contaminants and microorganisms to the surface and therefore have an anti-fouling effect that helps to prevent the deterioration of photocatalytic properties.

Typically, coatings combining photocatalytic and superhydrophobic properties are produced using chemical methods, such as hydrothermal, liquid phase deposition, etc. Pulsed DC magnetron sputtering is a wellknown method for thin film deposition, and photocatalytic coatings in particular. In this work a reactive pulsed DC magnetron sputtering technique using a blended PTFE - titanium dioxide powder target was employed for the production of photocatalytic superhydrophobic coatings. The surface characteristics and photocatalytic properties of the deposited composite coatings were studied with Raman spectroscopy, optical profilometry and scanning electron microscopy. Hydrophobicity was assessed through measurements of water contact angles, and photocatalytic properties were studied via methylene blue dye degradation under UV irradiation. It was found that variations of gas flow and, hence, process pressures allowed deposition of samples combining superhydrophobicity with stable photocatalytic efficiency under a UV light source. Reversible wettability behaviour was observed with alternating light-dark cycles.

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11:40am **F1-1-6 The Mechanisms of Growth of Zr-Fe-O Whiskers**, *Jingjing Gu*, University of North Texas, USA; *P Petry*, University of Rouen, France; *I Hammood*, *M Carl*, *R Reidy*, *S Aouadi*, University of North Texas, USA Ceramic whiskers are materials with high melting point, low density, good thermal and electric conductivity, and excellent corrosion-resistant materials. Whiskers are usually selected chosen as a reinforcing material in structural composites. In this presentation, whiskers were created by mixing and pressing nanopowders of ZrC, SiC, Y₂O₃, and Fe₂O₃ carbides. The nano-sized powders were then sintered at 1100°C for 6 hours, which resulted in the formation of Zr-Fe-O whiskers that were a few micometers in diameter and millimeters long. A model is proposed that accounts for the formation of these whiskers and for the thermodynamic processes that control whisker diameter.

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