Tuesday Afternoon, November 10, 2009

Advanced Surface Engineering
Room: C4 - Session SE+TF-TuA

Glancing Angle Deposition II
Moderator: K. Robbie, Queen's University, Canada

2:00pm **SE+TF-TuA1 Deposited Nanorod Films for Biosensor Applications**, ***W. Zhang***, University of Illinois at Urbana-Champaign, *S.M. Kim,* Chung-Ang University, Korea, *N. Ganesh,* Intel, *I. Block, P. Mathias, B.T. Cunningham*, University of Illinois at Urbana-Champaign **INVITED**

Planar photonic crystals have been used as the basis of many biological sensing devices. Here, we successfully demonstrated that the combination of the photonic crystal structures and a dielectric nanorod coating prepared by the glancing angle deposition technique can lead to significant increases in the device sensitivity.

By incorporating a TiO_2 nanorod coating onto the label-free biosensor structure, the surface area of the device is increased. The sensitivity of high surface area sensors is compared with sensors without the high surface area coating. Results for detection of polymer films, proteins, and small molecules indicate up to a seven-fold enhancement of detected adsorbed mass density.

When a TiO_2 nanorod coating is applied on top of the high index layer of an enhanced fluorescence biosensor, the emission intensity of a fluorescent dye on the device is increased by over one hundred times compared to a reference glass slide. The increased sensitivity is due to the combined effects of enhanced near-fields and enhanced surface area. The sensitivity is further increased by close to two hundred times when a TiO_2 nanorod film is used as the high index layer of the photonic crystal structure.

The planar photonic crystal is also combined with a SiO_2–Ag "post-cap" nanostructure for applications in surface-enhanced Raman spectroscopy (SERS). It is demonstrated that the resonant near fields of the photonic crystal could be used to efficiently couple light from a laser to the Ag nanoparticles to achieve a high SERS enhancement factor.

2:40pm **SE+TF-TuA3 Surface Enhanced Raman Scattering from Silver Nanorod Array Substrates: Characteristics and Origin**, ***Y. Liu***, *Z. Zhang, R.D. Dluhy, Y. Zhao*, University of Georgia

Surface-enhanced Raman scattering (SERS) has been a powerful analytical tool in chemical and biosensing applications. Silver nanorod array fabricated by oblique angle deposition can give a very strong SERS enhancement ($>10^8$). The SERS enhancement depends strongly on the length of nanorods, the incident angle of excitation light, the polarization states of excitation light, and the reflectance from substrate. A modified Greenler's model based on the reflection from a single Ag nanorod and the substrate as well as dipole radiation is proposed to explain these SERS characteristics. The theoretical calculation qualitatively agrees well with the experimental results. However, the location of the strongest SERS enhancement and the nature of such an enhancement are still unknown. To answer this question, we have designed another set of experiments, by taking the advantage of oblique angle deposition, to put Raman probe molecules on different locations of Ag nanorod array substrates and found that the apparent SERS enhancement factor is about 50 ~ 200 times from the surface of the nanorods than that from the Ag thin film surface under Ag nanorods array. These effects cannot be interpreted directly by the local electric field enhancement effect. By combining the local electric field effect calculated by three dimensional finite-difference time-domain method and the anisotropic optical absorbance of the SERS signal from the anisotropic Ag nanorod array, the numerical calculations are semi-quantitatively agree with the experimental results.

* This work is supported by National Science Foundation (NO. ECS-0701787) and US Army Research Laboratory (W911NF-07-2-0065).

References:

Y. -J. Liu, J. -G. Fan, Y. -P. Zhao, S. Shanmukh, and R. A. Dluhy, *Angle Dependent Surface Enhanced Raman Scattering Obtained from a Ag Nanorod Array Substrates*, Appl. Phys. Lett. 89, 173134 (2006)

J. D. Driskell, S. Shanmukh, Y. -J. Liu, S. B. Chaney, X. J. Tang, Y. -P. Zhao, and R. A. Dluhy, *The Use of Aligned Silver Nanorod Arrays Prepared by Oblique Angle Deposition as Surface Enhanced Raman Scattering Substrates*, J. Phys. Chem. C 112, 895 (2008)

Y. -J. Liu, Y. -P. Zhao, *Simple Model for Surface-enhanced Raman Scattering from Tilted Silver Nanorod Array Substrates*, Phys. Rev. B 78, 075436 (2008)

Y.-J. Liu, Z.-Y. Zhang, Q. Zhao, R. A. Dluhy, and Y.-P. Zhao, *The Surface Enhanced Raman Scattering from Ag Nanorod Array Substrate: the Site Dependent enhancement and Layer Absorbance Effect*, J. Phys. Chem. C, in press (2009)

3:00pm **SE+TF-TuA4 Local Plasmon Resonators Combinatorially-Multilayered by Oblique Angle Deposition Technique**, ***M. Suzuki***, *R. Tabuchi, Y. Imai, S. Li, K. Nakajima, K. Kimura,* Kyoto University, Japan, *T. Fukuoka*, Archilys RP, Japan

We have successfully prepared multilayered sculptured thin films with various combinations of the layer thicknesses using a shutter system specially designed for the oblique angle deposition. A series of different thicknesses were realized on a single substrate by moving a step-shaped shutter incrementally across the sample during the oblique angle deposition, while an ordinary straight shutter was used during normal deposition. This deposition process has been applied to fabricate local plasmon resonators comprised of the sandwich of Au nanorod array (NRA)/structured dielectric layer/Ag mirror. The fundamental optical properties of the local plasmon resonators have been already reported [1]. Briefly, the reflectance in NIR region can be controlled between 10^{-4} and 1 due to the strong interference. At low reflectance conditions, Au nanorods absorb most of the incident light and are expected to enhance the local electric field in their close vicinity. However, detailed relation between the optical properties of the local plasmon resonators and the combination of the thicknesses of Au and dielectric layers has never been clarified. In this study, we prepared 4x6 arrays of the local plasmon resonators which have four and six different thicknesses of Au and the dielectric layers, respectively, on a single substrate of 50x50 mm^2. The surface enhanced Raman scattering intensity measured on the element with low reflectance is about 50 times stronger than that on the Au NRA prepared on the glass substrate (without Ag mirror). This indicates that the local electric field in the NIR region is controllable by using interference. Therefore, the NRA fabricated on the mirror with appropriate spacer layers is useful not only for improving conventional biochemical sensing but also for the novel applications using spatiotemporal control of the local plasmons. For optimization of the multilayered sculptured thin films, the combinatorial approach is quite useful.

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

4:00pm **SE+TF-TuA7 Influence of Substrate Temperature on Glancing Angle Deposited Ag Nanorods**, ***C. Khare***, *C. Patzig, J.W. Gerlach,* Leibniz-Institut of Surface Modification, Germany, *B. Fuhrmann,* Martin-Luther-University Halle, Germany, *B. Rauschenbach*, Leibniz-Institut of Surface Modification, Germany

When Ag sculptured thin films (STFs) were grown with glancing angle deposition by ion beam sputtering at either room temperature or elevated substrate temperatures T_S, an enormous topographical difference could be observed. The incident particle flux reached the silicon substrate at a glancing angle $\beta \geq 80°$ as measured to the substrate normal . A slit aperture was used in order to reduce the particle beam divergence. At room temperature, columnar structures were formed, irrespective of the presence of the slit aperture. At elevated temperatures (300° C, 350° C) and collimated particle flux in the presence of the slit aperture, however, accelerated surface diffusion causes the growth of nanorod- and nanowire-like structures. In the absence of the slit aperture, the flux beam divergence is higher, leading to island- and mountain-like crystalline structures that were found at elevated temperatures. The density of the nanorods and nanowires was observed to be higher on the planar Si substrates in comparison to honeycomb-like pre-patterned substrates with different pattern periods. On the patterned substrates, the nanorods are not necessarily found to be evolving on the seed points, but can rather also be observed in intermediate pre-pattern spaces. The glancing angle deposited films were observed to be polycrystalline, where the (111) crystal orientation of the film is dominant, while the presence of the less intense (200) reflection was noticed from XRD measurements. In contrast, the closed films deposited with $\beta \approx 0°$ at high temperatures were found to be epitaxial with (200) orientation.

4:20pm **SE+TF-TuA8 Temperature Driven Anomalous Scaling during Glancing Angle Deposition**, ***S. Mukherjee***, *D. Gall*, Rensselaer Polytechnic Institute

Ta, Nb, Cr and Al nanorod structures were grown by glancing angle physical vapor deposition on a continuously rotated Si(001) substrate at an incidence angle of 84° and at substrate temperatures T_s = 300-1125 K. The width w of the self-affine nanorods increases with the height h according to $w \alpha h^p$. The growth exponent p is a function of the homologous substrate temperature θ, which is the ratio of T_s to the melting point T_m. All studied

metallic systems exhibit the same $p(\theta)$ curve: p approaches a value of 0.5 for negligible surface diffusion ($\theta < 0.1$) and monotonously decreases to $p = 0.39$ for $\theta = 0.2$, as predicted by Meakin and Krug's model of nanorod growth with limited surface diffusion and by Mullins-Herring's model of 2+1 dimensional interface growth, respectively. However, p increases dramatically for $\theta = 0.22$-0.26, to reach an anomalous value of 0.71. Above the transition temperature $\theta_c = 0.24 \pm 0.02$, the growth exponent decreases to reach $p = 0.3$ at $\theta = 0.42$.

We present a semi-analytical model using mean-field nucleation and non-linear chaos theory that relates p with the exponential divergence λ from a surface diffusion limited material independent morphology that is controlled by atomic shadowing. p is a function of the average island separation distance $\langle s \rangle$, which is a measure of the diffusion length scale and varies with θ, the activation energy E_m for surface diffusion, the critical island size i, and the dimensionality of adatom surface diffusion. The model predicts a transition from a 2-d to a 3-d island growth mode at θ_c. This transition, in turn, exacerbates the chaotic bifurcation associated with the atomic shadowing by the islands on the nanorod growth fronts, resulting in the higher growth exponents above θ_c. The model also provides a single homologous activation energy $E_m/kT_m = 2.46$ for surface diffusion on curved nanorod growth fronts, applicable to all studied metallic systems at all temperatures. p follows a linear function with $\langle s \rangle$, in both high and low temperature regimes and the slope correlates with the slope of λ vs $\ln(h)$, indicating that the growth exponent and hence the morphology is intricately related to both shadowing and surface diffusion.

4:40pm **SE+TF-TuA9 Investigation of Surface Sensitivity of Relative Humidity Sensors through ALD Coated GLAD**, ***M.T. Taschuk***, University of Alberta, Canada, *K.D. Harris, J.M. Buriak, M.J. Brett*, NRC National Institute for Nanotechnology, Canada

We have been investigating the performance and optimization of nanostructured relative humidity (RH) sensors produced by glancing angle deposition (GLAD) [1 – 2]. GLAD offers significant advantages for sensor applications, including extremely large surface areas, response times as low as 50 ms, and the use of any material compatible with physical vapour deposition. However, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. Response time and magnitude varies with the size and nature of pores in our sensors, and the interaction between the analyte and deposited material. To better understand the analyte-surface interactions, we have studied the performance of RH sensors with a thin coating of TiO_2 deposited by atomic-layer deposition (ALD).

Columnar thin films of Si and TiO_2 were produced by GLAD on interdigitated electrode substrates, creating a RH sensor. The GLAD sensing layer was conformally coated with TiO2 films by atomic layer deposition. In this process, the deposition chamber is evacuated and the reactive precursor, titanium isopropoxide (TIPO), is admitted. A thin layer of TIPO saturates the exposed substrate surfaces, and once complete, the deposition chamber is purged and oxygen is introduced. At the precursor-loaded substrate, this oxygen reacts with TIPO in a plasma-driven process to produce a thin layer of TiO_2 conformally surrounding the high surface area GLAD film. In this work, the ALD process is repeated cyclically to build up TiO_2 layers of different thicknesses.

Preliminary investigations have used 1.5 µm Si and TiO_2 GLAD films, coated with ALD TiO2 films between 2 nm and 32 nm thick. The RH sensing properties of these devices were testing using a custom environmental chamber [1]. As expected, the uncoated Si and TiO_2 thins films exhibited different responsivities. However, once the different sensors were coated with ALD TiO2 layers as thin as 2 nm, sensor response was very similar, indicating that sensor function is dominated by surface properties. To better investigate the transition between the GLAD post dominated response and ALD-layer dominated response, a series of films with thinner ALD coatings is underway. The sensor response will be characterized as a function of RH, electrical probe frequency, and ALD layer thickness. Current experimental results will be presented.

[1] J.J. Steele et al. IEEE Sensors Journal (2008) Vol 8. pp. 1422 - 1429

[2] M.T. Taschuk et al. Sensors and Actuators B (2008) Vol. 134, pp. 666 - 671.

5:00pm **SE+TF-TuA10 Direct Measurement of Porosity in Glancing Angle Deposited Thin Films**, *A.R. Gonzalez-Elipe,* ICMSE (CSIC - U. Seville), Spain, ***F. Yubero***, CSIC, Spain, *J.R. Sanchez-Valencia*, ICMSE (CSIC - U. Seville), Spain

Porosity of thin films is generally estimated in an indirect way by looking to their refraction index. In the present communication we determine directly the porosity of the a series of glancing angle deposited films by measuring the adsorption/desorption of water as a function of the partial pressure of water vapour in contact with the film. The method consists of measuring the changes in the vibration frequency of a quartz crystal monitor (QCM) with its surface covered by the thin films.1 The analysis of the obtained curves permits to estimate the total porosity of the films, its partition between mesopores (pores larger than 2 nm) and micropores (pores smaller than 2 nm) and the pore size distribution function. Results are shown for a series of titanium oxide thin films prepared by evaporation at different glancing angles between 60º and 90º. It is shown that both the total porosity and the partition between meso and micropores change with the evaporation angle. A good correlation exists between these measurements and the optical constants of these films determined by ellipsometry. Analysis of the films by Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) gives some hints to account for the evolution of porosity as a function of the evaporation angle.

1) A. Borrás, J.R. Sánchez-Valencia, J. Garrido-Molinero, A. Barranco, A.R. González-Elipe, Microporous and Mesoporous Materials 118 (2009) 314-324

5:20pm **SE+TF-TuA11 Monoclinic Magnetic Anisotropy and Hybridization of GLAD Sculptured Thin Films**, *A. Kjerstad, D. Schmidt, T. Hofman,* ***M. Schubert***, *E. Schubert, R. Skomski, D. Sellmeyer*, University of Nebraska - Lincoln

We report on the magnetic monoclinic anisotropy behavior of cobalt sculptured GLAD structures. Exciting new physics are presented in a model showing the nanostructures result in a thin film with tunable properties dependent on orientation, tilt, and patterning of the slanted nanowires. These sculptured thin films can be further modified – non-magnetic structures are coated with ferroelectric polymers for novel surfaces. Alternatively, magnetic structures are modified using non-magnetic materials, once again creating hybridized structures with undiscovered properties.

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