IUVSTA WORKSHOP 68
Multifunctional Surface Engineering for Advanced Energy Applications
City University of Hong Kong, December 9-13, 2012.

The 68th IUVSTA workshop was held at the City Universityof Hong Kong, December 9-13, 2012 with 60 participants from 15 countries/regions: Canada, China, Czech Republic, France, Germany, Hong Kong, India, Japan, Mexico, Poland, Singapore, Sweden, Switzerland, Taiwan, USA.

The workshop was organized by the IUVSTA Surface Engineering Division (Chair Ivan Petrov) and the IUVSTA Thin Film Division (Chair Alberto Tagliaferro). The divisions gratefully acknowledge the superb organization by the local chair Juan Antonio Zapien and co-chair Wenjun Zhang from the Center of Super-Diamond and Advanced Films, Department of Physics and Materials Science, City University of Hong Kong, Hong Kong. The international advisory committee had members: Dechun Ba, Northeastern University China, China, Francois Flory, Univ. Paul Cézanne, France, Claes Granqvist, Uppsala University, Sweden, Cheng Chung Lee, National Central University, Taiwan, Phillip J. Martin, CSIRO, Australia, and Ludvik Martinu, Ecole Polytechnique Montréal, Canada.

The IUVSTA funds were used fully to cover in part the registration fee for the invited speakers. The budget was break-even. This was possible due the sponsorship by seven vendors: Bruker, Teltec, J. A. Woollam, VG Scienta, Agilent Technologies, Renishaw, and Omicron.

INVITED SPEAKERS: (IN ALPHABETICAL ORDER)
Hynek Biederman, Charles University in Prague, Czech Republic
Fabio Cicoira, Ecole Polytechnique Montréal, Canada
Wolfgang Diehl, Fraunhofer IST, Brauschweig, Germany
Mariusz Dudek, Technical University of Lodz, Poland
Ali Erdemir, Argonne National Laboratory, USA
Francois Flory, Institut Materiaux Microelectronique Nanosciences de Provence (Im2np), France
Claes-Göran Granqvist, Uppsala University, Sweden
Ulf Helmersson, University of Linkoping, Sweden
Jiansheng JIE, Soochow University, China
Jolanta Klemberg-Sapieha, Ecole Polytechnique Montréal, Canada
Carl M. Lampert, Star Science, USA
Shu Ping Daniel Lau, The Hong Kong Polytechnic University, Hong Kong
Chun-Sing Lee, City University of Hong Kong, Hong Kong
Cheng-Chung Lee, National Central University, Taiwan
Guoqiang Li, South China University of Technology, China
Jian Lu, City University of Hong Kong, Hong Kong
Ludvik Martinu, Ecole Polytechnique Montréal, Canada
Stanislaw F. Mitura, Technical University of Lodz, Poland
Stephen Muhl, Universidad Nacional Autónoma de México, Mexico
Joerg Patscheider, Laboratory of Nanoscale Materials Science, EMPA, Switzerland
Ivan Petrov, University of Illinois, USA
Shyama Rath, University of Delhi, India
Clara Santato, Ecole Polytechnique Montréal, Canada
Jayati Sarkar, Indian Institute of Technology, India
Qing Shen, The University of Electro-Communications, Japan
Wanxin Sun, Bruker Nano Surfaces Division, Singapore
Shulin Sun, National Taiwan University, Taiwan
Wenhao Sun, Massachusetts Institute of Technology, USA

Roy Vellaisamy, City University of Hong Kong, Hong Kong
Chun Dong Wang, City University of Hong Kong, Hong Kong
Jianbin Xu, The Chinese University of Hong Kong, Hong Kong
Feng Yan, The Hong Kong Polytechnic University, Hong Kong
Siu Fung Yu, The Hong Kong Polytechnic University, Hong Kong
Juan Antonio Zapien, City University of Hong Kong, Hong Kong
Zijian Zheng, The Hong Kong Polytechnic University, Hong Kong

The delegates attending this workshop enjoyed extensive and very fruitful discussions during the following twelve topical sessions and three dedicated discussion session

Functional Materials I, II
Tribological Systems
Tailored Micro/Nano- Structures
Material Modeling
Smart Coatings I, II
Organic and Soft Matter I, II
Light for Mankind I, II, III
Discussion sessions: Challenges in Smart Photonic / Plasmoniccoating Systems
Discussion sessions I and II: Challenges in Surface / Interface Engineering

There was a poster session with 29 presenters from CityU, PolyU, USA, Taiwan, Mainland China. Three best poster awards were presented. At the opening of the workshop Ivan Petrov made a 10 min presentation on IUVSTA, the structure and activities of the Union.

Functional Materials

Steve Muhl described three novel modifications to existing plasma assisted thin film deposition methods . The first was a cylindrical geometry of the planar HRAVA system. The centre graphite anode was found to reach 1800oC after a few seconds of operation at an arc current of 200A. Using an Al cathode, almost macroparticle free films could be deposited at ~4 nm/s and >90% of the depositing species were ions. The cylindrical geometry allowed the easy application of a magnetic field to the complete system; however the effect of the field was complex and only clearly affected the ion flux to the substrate. Using a partial pressure of 10mtorr of air it was possible to deposit Al_2O_3. The second system involved the plasma assisted formation of silicon or germanium hydride followed by the thermal decomposition of the hydride to form a Si or Ge, thin film. The system was used to produce Mo and Ta hydride in a dense RF or pulsed-DC H_2 plasma formed in a hollow cathode lined with the respective metal. The hydride was then thermal decomposed at >300oC to form the corresponding metal film. The third system was a torroidal planar geometry of a hollow cathode made of graphite and was connected to a 250 kHz pulsed-DC supply. Pieces of Bi were placed inside the cathode and sputtering by Ar rapidly distributed this element over the interior surface of the cathode. The deposition rate increased with; decreasing substrate-cathode separation or gas pressure, as well as, increasing plasma power or gas flow.

Wolfgang Diehl made a comprehensive review of recent advances in functional coatings produced by plasma processes which help build superior products in nearly all industrial branches. He convered a wide range of technologies DC Magnetron sputtering, PACVD, Hollow Cathode Gas Flow Sputtering used to deposit DLC, TCO deposited by HIPIMS, and plasma processes to make TiO2 coatings. A lot of details of the effect of inclusion of component X in a-C:H:X coatings and multilayer a-C:H structures. Properties of c-BN but few fabrication details. Fraunhofer has developed an in-house deposition simulation software. Applications hard coatings, sensors, PV & displays, photo induced hydrophil/phobicity, photo catalysis. Atmospheric plasmas for surface functionalization for adhesion, biomolecules, flexible electronics.

Ulf Helmersson reviewed pulsed plasma processes which open up for the use of very high plasma densities in synthesis of materials. Such high plasma densities in turn lead to a high degree of ionization of the deposition material. With higher voltage-shorter pulses get a higher degree of ionization which allows better control of the energy and direction of ion incidence. An increased coverage of adatoms during high intensity pulsing means you get more nucleation and this can increase the film density. These results are due to the energetic self-ion-bombardment, the very high nucleation rates, or a combination of the two. An alternative is the use Ne rather than Ar this gives a higher electron temperature and therefore, more ionization. Use pulsed (700Hz, pulse length 30ms, peak current 30A at 100Pa) hollow cathode sputtering to form nanoparticles. In the highly ionized gas you get nucleation, then coagulation, followed by particle growth. The particles can capture electrons, accumulate a negative charge causing mutual repulsion and trapping of positive ions; much more than for neutral particles. Can get nanoparticle sizes from 10 to 40nm as the frequency was increased from 500 to 1300Hz. Addition of He to the gas (plasma cooling) can change the nanoparticle size and shape.

Joerg Patscheider reviewed recent progress on optically transparent abrasion resistant coatings. For such applications thin films with enhanced hardness based on Al-X-N with additions of X = Si, Ge or Sn are attractive candidate materials, as they can be prepared to be optically transparent. Enhanced hardness of more than 30 GPa is observed in Al-Si-N, but instead of a typically sharp hardness maximum observed in transition metal nitrides/silicon nitride nanocomposites, a broad hardness maximum exists as a function of the silicon content in the layers. The optical characteristics, stress, hardness, wear rate and corrosion resistance all change. The inclusion of oxygen, depending on the Si%, can improve the film morphology and hardness.The choice of the additional X element allows depositing highly transparent coatings for the case of Si and the control of color in the range from yellow to red by the tuning of the UV absorption edge in the case of Ge and Sn. In these systems enhanced hardness can be obtained at certain concentrations of Si or Ge, respectively. Using HiPIMS with its high ion flux and ion energy the properties of Al-Si-N coatings were improved.

Stanislaw Mitura described the modification of the surface of diamond through a plasma chemical reaction in a MW PACVD rotary reactor system. This was found to be much better than the commonly used methods. Evaluation of the biological properties of modified ND was performed by the analysis of ND – tissue interaction.

Chun Dong Wang employed microwave plasmas were employed to synthesize single- or double-layer large scale graphene sheets on copper foils using solid carbon sources, polymethylmetacrylate (PMMA) and Polydimethylsiloxane (PDMS). The utilization of reactive hydrogen plasmas enable the growth of graphene at reduced temperatures as compared to conventional thermal chemical vapour deposition processes. The effects of substrate temperature on graphene quality were studied by analysis of the Raman spectra, and a reduction of defects at elevated temperatures was observed. Additionally, this approach facilitated the incorporation of nitrogen into the graphene by plasma treatment using a nitrogen/hydrogen gas mixture.

Tribological Systems

Ali Erdemir reviewed his results in the exploration of the possibility of designing catalytically active nanocomposite coatings that can derive diamondlike carbon based boundary films directly from lubricating oils. For this purpose, they designed a series of catalytically active nanocomposite coatings on steel substrates by adjusting the ratios of the softer catalytic phases (made out of known catalysts, such as Pd, Ag, Cu, Ni, etc.) and a harder nitride phases of Mo, W, V, and Re, etc. which are also catalytically active. When such films were synthesized and tested on sliding tribological surfaces under lubricated sliding conditions, they were able to extract carbon-based boundary films from the lubricating oils and deposit them as protective boundary films on the rubbing surfaces. Using UV Raman and a variety of other surface and structure analytical techniques, they were able to confirm that these boundary films were similar to diamondlike carbon (DLC). Some of the main characteristics of DLC boundary films extracted from lubricating oils were: very low friction coefficients (less than 0.05) even under extreme sliding conditions and very high resistance to wear and scuffing.

Jolanta Sapieha outlined the approaches that allow one to design and fabricate high-performance protective coatings: need to understand the details of the erosion, wear and corrosion processes. Improve these properties you get good energy savings. Studies included stainless steel or titanium alloy substrates coated with protective systems consisting of single- or multilayer architectures of metal nitrides and carbides (e.g., TiN, TiC, CrN) and nanocomposites (TiN/SiN, TiCN/SiCN, TiSiN, CrSiN) by pulsed magnetron sputtering or by plasma enhanced chemical vapor deposition. Applications include aircraft engine components, cutting tools, and biomedical implants.

Smart Coatings

C. G. Granqvist presented an overview of surface angineering challenges for development of chromogenic coatings for energy efficient buildings. He outlined basic device designs, device performance, pertinent materials and their thin film deposition technologies. There are two chromogenic technologies: *thermochromics* which allows the transparency to decrease when the temperature exceeds a certain comfort level, and *electrochromics* which enables electrically controlled changes of the transparency between widely separated extrema. Nanostructured coatings of VO2 by sputtering give angular dependence to the optical properties.

Feng Yan from the Hong Kong Polytechnic University described the CVD process optimized for the growth of single layer graphene, which has been used to fabricate graphene transistors have been successfully used as highly sensitive infrared sensors. Photodetectors based on single-layer CVD-grown graphene and PbS quantum dots are fabricated by solution process, which show ultrahigh responsivities up to 107 A/W under infrared light illumination. The devices fabricated on flexible plastic substrates show excellent bending stability. Also the conductance of single-layer graphene was increased for more than 400% when it was doped with Au nanoparticles and poly(3,4-ethylenedioxythiophene): poly(styrene sulfonic acid). Semitransparent organic solar cells were fabricated with efficiencies up to 3%.

Tailored Micro/Nano- Structures

Hynek Biederman describe a novel system for production of nanoparticles by sputtering in a cluster source, i.e. by sputtering from a target in an enclosed space at relatively high pressure, up to 140Pa, where the gas is significantly cooled by the side walls of the container and the nanoparticles are driven through a small, 1.5mm diam., aperture in the end wall of the container by the flow of Ar into the deposition chamber which is at a lower pressure (0.2Pa). Various metal nanoparticles such as Ag, Cu, Al and Pt etc. were produced. Ag and Al nanoparticles were embedded into C:H plasma polymer in order to prepare nanocomposite films Ag/C:H and Al/C:H. Using a graphite target and Ar + n-hexane or a Nylon 6,6 or PTFE targets with Ar the deposit is a polymer of the C:H, or the respective target material. The polymer targets can be used to cover Ag nanoparticles to produce nanocomposites, with properties ranging from superhydrophylic y superhydrophobic depending on the size of the nanoparticles.

Mariusz Dubek presented different microstructures, obtained in MW CVD diamond using a Nd:YAG laser with wavelength 355 nm, a pulse time of 20-35 ns, different powers (max 5kW), scan speeds (50-400 mm/s) and scan grids (5-20 μm). Microstructures with wide range of geometries were obtained. Raman spectra show that the diamond after laser treatment was unchanged (Raman diamond peak is only slightly wider and sometimes slightly shifted) or can be modified (Raman spectra showing disorder with the appearance of additional peaks such as diamond-like or graphite materials). Modification of the diamond in specific places of the sample together with the microstructuring, gives the possibility of new applications because the material after interaction with laser light can have it's physical and mechanical properties altered in specific places. The precise geometries of the microstructures, perpendicular, deep channels and smooth surfaces showed that laser induced ablative etching technique of diamond can probably be applied to a various applications.

Ivan Petrov described the growth of vertically aligned a-SiO_2 nanowires (diam. 5-10nm) by a low-temperature (190oC), ion-enhanced, reactive vapor–liquid–solid (VLS) method over large areas of any substrate on to which a thin silicon film could be deposited. A self-organized layer of molten indium droplets (30-300nm diam.), produced by substrate heating (needs a barrier layer of Si since In does not extensively wet Si). These act as a seed for the wire synthesis under magnetron sputter deposition of Si (in Ar + H_2 + trace H_2O) with concurrent ion bombardment which enhances the mixing of oxygen and silicon into the indium and aligns vertically the growing nanowires. The vertical growth rate can reach up to 1000 nm-min^{-1} in an environment containing only argon and traces of water vapor. Silicon oxide precipitates from each indium seed in the form of multiple thin strands having diameters less than 9 nm and practically independent of droplet size. Spontaneous alignment of these stranded, free-standing wires toward a source of directional ion irradiation was proposed to be driven by local surface area minimization. The nanowire patterns over a wide range of angles can be formed by post synthesis irradiation by ion beams. Ion-induced orientation control and modification of nanowire arrays is a useful method for nanoscale surface engineering. The nanowires were coated with a number of materials, in various ways: a-Si for use as negative materials and LiMn2O4 for use in Li ion batteries.

Organic and Soft Matter

Chun Sing Lee describe the thin film processes and materials used in the fabrication of organic light-emitting devices (OLEDs). Specifically he described the interfaces formed between six different pairs of organic molecules which are known to give exciplex emissions. Exciplex emission is the radiative decay of charge transfer complex formed between two different organic molecules. Understanding the physics of exciplex emission permits to obtain high efficiency exciplex emission devices.

Clara Santato devoted her presentation to the physics of electrolyte gating as a platform to control the conductivity of nanostructured thin films. Electrolyte gating is used to fabricate transistors operating at low voltage (below 1 V) as an alternative to other approaches such the use of high-k, or ultrathin gate dielectrics.

In a related presentation, Fabio Cicoira made an overview of the increasing use of organic electroactive to engineer flexible, low-cost and easily processable electronic devices, such as organic light-emitting diodes, transistors and photovoltaic cells. He outlined the material and think film deposition challenges in the fabrication of organic electrochemical transistors (OECTs). This class of devices particularly attractive for applications in bioelectronics as sensors for hydrogen peroxide, glucose, dopamine, chloride ions, cells and bacteria.

V. A. L. Roy outlined the need to develop stable organic semiconductors exhibiting broad solar spectral coverage to enhance the generation of excitons and better charge carrier transport properties. He presented a ternary system that consists of insoluble organic nanocrystals in donor-acceptor polymer blends. He described a simple solution process technique for the formation of an organic/organic composite has many advantages for device application.

Miniaturizations of patterns on soft elastic films are important in a host of technological applications ranging from flexible electronics, opto-electronics, microfluidics, micro-electromechanical systems etc.

Jayati Sarkar describe two novel surface engineering approached for in miaturizations of patterns on soft elastic films used in microelectromechanical systems.

These include soft elastic bilayers instead of a single elastic film and using a patterned substrate instead of a flat substrate with a single elastic film cast on top.

Light for Mankind

Cheng-Chung Lee outlined novel surface engineering approaches to form antireflection coating for silicon based solar cell. Since the Fresnel reflection loss can be higher han 30% nano-structured coatings to reduce such loss have been proposed. Two kinds of novel structures for antireflection are investigated: (i) nanosphere lithography was used to fabricate shapes of frustum, bullet, and pyramid array with high aspect ratio. The period of nano-structure was 600 nm and the depth was under 1μm. The reflectance of silicon substrate was below 1.5% in the spectrum of 400-1000 nm. (ii) Another method to reduce the reflection loss is to use anodic aluminum oxide (AAO) method to fabricate a nano-cone array on the silicon substrate. The period of nano-cones was about 220 nm and the depth was 200-700 nm. The reflectance was reduced to less than 1% with the structure depth of 500-700 nm. Finally, the thin film solar cells were fabricated with above antireflection structures, and the efficiency of the solar cells increased 17.37% than those without antireflecion structures.

Guoqiang Li described innovatinve pulsed laser deposition (PLD) method which makes it possible to grow GaN and AlN thin films with abrupt heterointerfaces on chemically vulnerable materials at low temperatures, because the laser-ablated species impinge on the substrates with large kinetic energy that assists the surface migration of the film precursors on the surfaces thereby effectively suppresses the reaction of the interface between the epitaxial layers and the substrates, and reduces the thermal stress in thin films to some extent.

C.M. Lampert covered functional coatings and technology for advanced building applications. One important type of materials are electrochromic materials consisting of layered metal oxides in an electrolyte or solid ion conductor which have transport and charge storage characteristic similar to a battery structure. The structure consists of electrode/electrochromic/ion conductor/ion storage/electrode/glass in a thin film structure. Coloration of the films is achieved by both charge and ion movement. By film nano-engineering various visible and near-infrared responses can be induced, along with performance gains.

Shulin Sun reported on the design and experimental verification of plasmonic gradient meta-surfaces with high-efficiency anomalous reflection for visible. Compared to previously fabricated gradient meta-surfaces in infra-red regime, the samples work in a shorter wavelength regime with a broad bandwidth (700-900nm), exhibit a much higher conversion efficiency (~80%) to the anomalous reflection mode, and keep light polarization unchanged after the anomalous reflection. The findings may lead to many interesting applications, such as anti-reflection coating, polarization and spectral beam splitters, high-efficiency light absorber, and surface plasmon coupler.

Material Modeling

Ludvik Martinu outlined the approaches that allow one to design and fabricate high-performance coatings based on the understanding of the film growth mechanisms, on the lessons learned in the area of optical coatings (such as optical interference filters), and the process and materials modeling. He described recent studies of the ion-surface interactions in plasma environments, including bias- and pulsecontrolled PECVD and PVD techniques. He demonstrated the importance of ion-induced effects resulting in rapid structural and compositional changes below film or substrate surfaces, as well as significant self-organization, ion mixing and interface broadening, and relocation of a large proportion of deposited atoms below the growth surface. He presented specific examples of the discrete and graded optical coating designs, process control and monitoring strategies, and performance assessment, including optical security interference structures for the protection of banknotes and precious documents as well as for energy saving, smart radiators for the thermal control in satellites, optical thin film sensors, transparent conductive oxide electrodes and others.

Jian Lu presented the basic concept of surface nanocrystallization of metallic materials and the recent developments of the SMAT (Surface Mechanical Attrition Treatment) are presented. Significant enhancements in mechanical properties of the nanostructured surface layer in different materials will be analyzed. The effects of surface nanostructures on the mechanical behavior and on the failure mechanism of metallic material show the possibility to create structural materials of high yield strength and yet high ductility. The simulation of SMAT process using the finite element methods is compared with the experimental investigation using high speed camera. The computational models provide valuable information about the mechanical behavior of nanostructured layered composite material and show the mechanisms of the simultaneous enhancement of the ductility and the strength. Based on the new concepts developed for toughening the high strength materials, three new categories of high strength and high ductility materials have been realized based on the laminated nanostructured materials, high density nanotwins materials and surface nanocrystallization of BMGs.

J. A. Zapien described a very powerful novel technique Finite Difference Time Domain (FDTD) simulations which in combination with spectroscopic ellipsometry (SE) measurements offer a powerful synergetic approach for advanced nanoscale characterization. Light effects in nanostructures were solved for the particular case of Quantum Dot Sensitized Solar Cells (QDSCs) based on ZnO nanostructures.

There were plenty of opportunities for interactions during the coffee break lunches and the evening program which included an opening reception, see food dinner and the workshop banquet. The seefood dinner was part of a bus trip along Clear Water Bay Peninsula in Sai Kung, to Po Toi O, home to a traditional fishing village and one of the most famous restaurant “Seafood Island”. The workshop banquet was held at Shanghai Min in Tsim Sha Tsui, Kowloon. From the restaurant the workshop participants enjoyed the “Symphony of Lights”, the nightly multimedia show, which involves more than 40 buildings on both sides of the harbor.