The 2\textsuperscript{nd} International Thin Films Workshop
was held in Chongqing University, China

The 2\textsuperscript{nd} International Thin Films Workshop, co-organized by the Thin Films Society (TFS) and Chongqing University (CQU), was held on 13\textsuperscript{th} July 2013 in CQU, China. Over 20 participants from China, Australia, England, New Zealand, and Singapore attended the workshop. A wide range of topics was presented and discussed, including thin films and coatings for tribological, biological, energy, environmental, and microelectronic applications.

The Workshop organizers would like to express their sincere gratitude to the local host, CQU, for providing excellent service and premises. In particular, deep appreciation is due for Prof. Bai Chengguang, Vice Chairman of CQU council, Prof. Liu Qing, Vice President of CQU, Prof. Huang Jiamu, Executive Vice Dean of the School of Materials Science and Engineering, and Prof. Xin Yunchang, faculty member of the School of Materials Science and Engineering. The great hospitality has contributed to the success of the workshop.

The TFS executive committee members and its overseas Vice Presidents who were present in the workshop also discussed the venue and dates for the 7\textsuperscript{th} International Conference on Technological Advances of Thin Films & Surface Coatings (Thin Films 2014). It was agreed that Thin Films 2014 will be held in Chongqing during 15-18\textsuperscript{th} July 2014, again co-organized with Chongqing University. For more details, please refer to the TFS website at http://www3.ntu.edu.sg/mae/ThinFilmsSociety/.
Workshop scene - 1

Workshop scene - 2
Group photo

Night view of Chongqing City
Abstract Book
2nd International Thin Films Workshop
- Frontiers in Thin Films Technology -

Agenda – Oral contributions
Saturday 13th July 2013

Session 1: Chair Zhong Chen

8:30 am - 8:50 am: Chairman's welcome and general remarks, Professor Sam Zhang

8:50 am - 9:10 am: Tube-Whisker Nanostructures of TiO₂ with Superhydrophobic Properties, Wei Gao

9:10 am - 9:30 am: Reducing Graphene Oxide to Graphene by Vitamin C for Dye-Sensitized Solar Cell Photoanodes, Hui Ding

9:30 am - 9:50 am: Smart Thin Films and Nanostructures for MEMS, Biomedical and Integrated Microfluidic Biosensing Applications, Yongqing Fu

9:50 am - 10:30 am: Coffee break

Session 2: Chair Guojun Qi

10:30 am - 10:50 am: Micro-nano TiO₂ Films for Light Induced Cell Detachment, Kui Cheng

10:50 am - 11:10 am: The Influence of Helium Ion Irradiation on Amorphous Hydrocarbon Films, Dongping Liu

11:10 am - 11:30 am: Ti-Al-PTFE Anti-sticking Coatings, Erjia Liu

11:30 am - 11:50 am: Towards Hard yet Self-lubricious CrAlSiN Coatings, Yuexiu Qiu

11:50 am - 1:00 pm: Lunch

Session 3: Chair Dongping Liu

1:00 pm - 1:20 pm: Electrochemical Treatment of Concentrated Organic Wastewater, Zhaohong Huang
1:20 pm - 1:40 pm: The Optimization of the Deposition Parameters to Prepare ZnSnO$_3$ and Cd$_2$SnO$_4$ by RF Magnetron Sputtering from Powder Targets, Yanwen Zhou

1:40 pm - 2:00 pm: Close-looped FeGa/BaTiO$_3$/FeGa Sandwich Structure for High Magnetoelectric Effect, Zhaofu Du

2:00 pm - 2:20 pm: Ta-based Amorphous Metallic Thin Films for Copper Diffusion Barrier Application, Zhong Chen

2:20 pm - 3:00 pm: Coffee break

Session 4: Chair Sam Zhang

3:00 pm - 4:30 pm: Discussion of ThinFilms2014

4.30 pm: Close of Workshop
Organising Committee

Chairman

Professor Sam Zhang, Nanyang Technological University, Singapore, and President, Thin Films Society

Local Chair: Professor Liu Qing, Vice President, Chongqing University, China
Co-Chair: Professor Liu Erjia, Nanyang Technological University, Singapore, and Vice President, Thin Films Society

Members

Chen Zhong (Nanyang Technological University, Singapore)
Feng Bo (student, Chongqing University, China)
Huang Jiamu (Chongqing University, China)
Huang Xiaoxu (Chongqing University, China)
Lu Liangchen (student, Chongqing University, China)
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Tube-Whisker Nanostructures of TiO$_2$ with Superhydrophobic Properties

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Self-organized TiO$_2$ hierarchical nanostructures were fabricated by electrochemical anodization. The surface structure exhibited superhydrophobic behavior after coating with organic monolayers. Its hydrophobic property was further enhanced by increasing the porosity of TiO$_2$ nanostructure with an ultrasonic treatment, resulting in an extremely high water contact angle of 172.4°. We showed that the modified Ti mesh with superhydrophobic surface exhibited an interesting floating behavior on water that may have potential applications as aquatic devices.

Figure Caption: FSEM images of disordered TiO$_2$ nanowires (a); ordered TiO$_2$ nanotubes after the top layer was removed (b); contact angles of TiO$_2$ layers with different topographies after modified by organic monolayers (c); and topography transformation from nanowires (NW and NWNT) to nanotubes (NT) with ultrasonic treatment (d).

Acknowledgements: The authors would like to thank the contributions from X. Ouyang, J. Han and W. Qiu.
Reducing Graphene Oxide to Graphene by Vitamin C for Dye-Sensitized Solar Cell Photoanodes

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To enhance the efficiency of dye-sensitized solar cells (DSSCs), graphene flakes were introduced as 2D bridges into the nanocrystalline electrodes of DSSC for a high electron transport speed and high specific surface area.[1] As graphene is easily oxidized and usually exists in the form of graphene oxide, it is necessary to reduce the graphene oxide back to graphene in application. Hydrazine and its derivatives are often used as the reducing agent.[1,3] As hydrazine is toxic, environmentally benign chemicals are explored.[3] Vitamin C can be used to reduce graphene oxide to graphene. Error! Reference source not found. The obvious advantage of vitamin C as reducing agent is that having a mild reductive ability and nontoxic property. This paper studies graphene oxide reduction into graphene via vitamin C and mix with TiO₂ nanoparticles (P25) to uniformly disperse on the surface of graphene flakes to form graphene-P25 composite films as photoanode for DSSCs. The incorporation of graphene significantly improves the conductivity of the TiO₂ nanoparticle film and the conversion efficiency.

Key words: graphene flake, TiO₂ nanoparticle, Vitamin C, dye-sensitized solar cell, photoanode

Smart Thin Films and Nanostructures for MEMS, Biomedical and Integrated Microfluidic Biosensing Applications

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This talk will discuss about recent work on piezoelectric ZnO films for acoustic wave-based microfluidics and bio-sensor applications, as well as thin film shape memory alloy and shape memory polymer for microsurgery and microactuator applications. Piezoelectric ZnO film based acoustic wave devices can be successfully used as bio-sensors, based on the biomolecule recognition using highly sensitive surface acoustic waves and film bulk acoustic resonator devices. The acoustic wave generated on the ZnO acoustic devices can also induce significant acoustic streaming, small scale fluid mixing, pumping, ejection and atomization or nebulisation, particle concentration, cell manipulation, etc. The potential to fabricate an integrated lab-on-a-chip diagnostic system based on these ZnO acoustic wave technologies is introduced. Applications of nanowires on the ZnO based lab-on-chip are also discussed. TiNi thin film based microactuators become the actuator of choice in many aspects in the rapidly growing field of MEMS, microsurgery, and biomedical applications, Different types of TiNi thin film based microdevices, such as microgrippers, microswitches, micro-valves and pumps, microsensors are described and discussed. Recently, shape memory polymer and nanocomposites have also been applied in microactuation, microsurgery and tissue and cell applications. Its low cost and non-vacuum preparation method could find wide industry applications.

Micro-nano TiO$_2$ Films for Light Induced Cell Detachment

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Cell sheet technology attracts more and more attentions in recent years. Cells were firstly cultured in a dish to be a cell sheet consists of cells and extracellular matrix, and then be harvested completely. To do this, a special cell culture dish is needed. So far, the most prevalent dishes are based on temperature-sensitive polymer modified surface. Such surface is rather hydrophobic at the culture temperature and turns into hydrophilic when temperature goes down. Cells cultured on such surface could detach spontaneously at lower temperature owing to the wettability variation. In this way, a complete cell sheet with both cells and extracellular matrix could be obtained and directly used for implants. However, it was found the lowered temperature, which is inevitable during cell detachment, may impose some detrimental effects on cells activity. In our previous work, a photo-responsible surface was developed for such cell sheet tissue engineering application. Titania nanodots film were prepared through a sol-gel phase separation assemble method, the effect of nanodots parameters on wettability, light absorption and cell attachment were investigated. It was found after certain time of cell culture, a continuous cell sheet could form, and easily detached after 30 min UVA irradiation. The detached cells showed good activity and could be used for further cell culture. Such photo responsible nanodots film showed good potential in cell sheet tissue engineering application. In this work, the effect of modification of nanodots on cells detachment, as well as the detachment mechanism of light induced cells detachment was investigated and discussed.
The Influence of Helium Ion Irradiation on Amorphous Hydrocarbon Films

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Amorphous hydrocarbon films were irradiated with 60-140 keV He ions at the dose ranging from 1.0×10¹⁵ to 1.0×10¹⁷ ions/cm². The films about 1.4 µm thick were deposited on Si substrates and irradiated at room temperature. The surface and mechanical properties of as-deposited and He ion irradiated hydrocarbon films were analyzed by using atomic force microscopy (AFM), AFM-based nanoindentation and scratching tests. Their chemical compositions and structural properties were evaluated by FTIR and Raman measurements. Analysis showed that the He ion irradiation led to a decrease in their surface roughness and an increase in the nanohardness and scratching resistance. FTIR measurements indicated that the content of bonded H atoms in hydrocarbon samples was greatly decreased due to the He ion irradiation, and the dense and covalent three-dimensional network was formed in films. The Raman data confirmed the microstructural evolution of samples into a dense metastable structure containing a large fraction of sp² C clusters. Polymer-like hydrocarbon films were irradiated with 100 keV He⁺ or annealed at sample temperatures varying from 25 to 600 °C. The effects of sample temperature on the structure and nanohardness of hydrocarbon films are investigated by atomic force microscopy (AFM), AFM-based nanoindentation, Fourier transform infrared spectroscopy, and Raman spectroscopy. Analysis shows that annealing results in the decrease in the nanohardness of hydrocarbon films from 4.0 GPa to 0.55 GPa while He⁺ irradiation at an elevated sample temperature results in the formation of dense diamond-like carbon films with nanohardness up to 20.0 GPa. This indicates that polymer-like hydrocarbon films can be transformed into the hard diamond-like carbon films with a relatively low H content on vacuum vessels of fusion devices due to the energetic bombardments at an elevated wall temperature. Analysis indicates that He ion irradiation results in the evolution of polymer-like hydrocarbon into a dense structure containing a large fraction of sp² carbon clusters. The sp² carbon clusters formed in irradiated hydrocarbon films can contribute to the formation of filament-like emission channels with a relatively high local field-enhancing factor.
Ti-Al-PTFE Anti-sticking Coatings

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Stainless steel micromold is an alternative of silicon micromold in the fabrication of polymeric microfluidic devices because of the brittleness and short lifetime of silicon mold. High adhesion and friction of stainless steel micromold can cause the distortion of the microstructures of polymeric products. In this work, titanium (Ti), aluminum (Al) and polytetrafluoroethylene (PTFE) were co-sputter deposited on stainless steel micromolds to improve their surface properties. The sputtering power applied to the PTFE target was varied to control the PTFE concentration in the Ti–Al–PTFE coatings, which affected the bonding structure, surface roughness, friction and contact angle of the coatings characterized using Raman spectroscopy, X-ray photoelectron spectroscopy, confocal microscopy, ball-on-disc tribometer and optical tensiometer, respectively. It was observed that the Ti–Al–PTFE coatings were a mixture of carbide, PTFE-like material and amorphous carbon. The surface roughness of coated micromolds decreased with the increase in PTFE concentration. The Ti–Al–PTFE coating deposited with 50 W sputtering power applied to the PTFE target showed the lowest friction coefficient and surface energy of about 0.17 and $13.1 \times 10^{-3}$ N/m, respectively. The coated stainless steel micromolds showed a better replication performance compared to the bare stainless steel micromolds in terms of the quality of polymeric microfluidic devices fabricated using hot embossing process. This work also investigated the coating properties at the sidewalls of the micromold channels and the limitations of the Ti–Al–PTFE coatings for application in hot-embossing.
Towards Hard yet Self-lubricious CrAlSiN Coatings

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CrAlSiN coating is hard with excellent wear and oxidation resistance but lack of lubrication. Vanadium nitride (VN) is easily oxidized to form vanadium oxides and becomes lubricious under stress. Incorporating VN into CrAlSiN to form CrAlSiVN coating renders both hardness and self-lubrication in dry machining.

This study investigates the effect of vanadium content on hard yet self-lubricious coating’s mechanical and tribological properties. The coatings are deposited on cemented tungsten carbide and Si wafer (100) substrates in an in-line magnetron sputtering system. Grazing incidence X-ray diffractometer, scanning electron microscopy, atomic force microscopy, electron probe micro-analyzer and X-ray photoelectron spectroscopy are employed to characterize the microstructures and chemistry. Nanoindentation and ball-on-disc tribo-tester are used in characterization of the mechanical and tribological properties. The coatings demonstrate lubriciousness of coefficient of friction with tungsten carbide from 0.55 down to 0.39 with acceptable loss of hardness (from 34.8 GPa down to 29.4 GPa).
Electrochemical Treatment of Concentrated Organic Wastewater

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Large amount of concentrated organic wastewaters is generated from various industrial operations in pharmaceutical, textile, paper making, printing and dying, oil and gas companies. Treatment of such concentrated organic wastewater is a challenging issue. The widely used biological processes are ineffective for treatment of wastewater with lower BOD/COD ratio than 0.5 due to the presence of toxic and bio-refractory organic substances. Researchers have explored many approaches with physical, chemical, electrochemical and photocatalytic processes and concluded that, although no technology can compete with biological method in terms of cost effectiveness, some processes could be in good complement with the biological processes to provide a total solution. Electrochemical techniques are among such promising complementary options. This presentation will cover electrochemical treatment of organic wastewaters and the relevant research activities in SIMTech, focusing on the recent progress in anode material development for electro-oxidation.
The Optimization of the Deposition Parameters to Prepare ZnSnO$_3$ and Cd$_2$SnO$_4$ by RF Magnetron Sputtering from Powder Targets

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Transparent conductive oxide ZnSnO$_3$ and Cd$_2$SnO$_4$ films were prepared by radio frequency magnetron sputtering from powder targets. In order to achieve the combined optimum electrical and optical properties of ZnSnO$_3$ and Cd$_2$SnO$_4$, orthogonal experimental arrays on sputtering parameters, i.e. deposition power, chamber pressure and the separation between target and substrate, were designed and performed. The morphological structures of the ZnSnO$_3$ and Cd$_2$SnO$_4$ films were columnar in grain sizes over 100 nm. The domain sizes of the nanocrystals, consisting of columnar grains, were about 10 nm. The average transmittance of the films within the visible wavelength was about 80%. The cut-off points and the absorbance at 500 nm wavelength of the optical spectra varied with the deposition parameters. The electrical properties also changed with the processes. The carrier concentrations of the ZnSnO$_3$ and Cd$_2$SnO$_4$ films reached the order of $10^{20}$ and $10^{21}$ cm$^{-3}$, average mobilities, 25 and 48 cm$^2$V$^{-1}$s$^{-1}$, and resistivities about $10^{-4}$ and $10^{-5}$ Ω·cm, respectively. The optimized deposition processes of the ZnSnO$_3$ and Cd$_2$SnO$_4$ films presented here were 400 W-0.3 Pa-130 mm and 200 W-0.3 Pa-130 mm, respectively.
Close-looped FeGa/BaTiO$_3$/FeGa Sandwich Structure for High Magnetolectric Effect

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Close-looped FeGa/BaTiO$_3$/FeGa sandwich structure was fabricated to improve the magnetolectric effect of the two-phase magnetoelectric system. The magnetoelectric voltages and coefficients have been characterized under a static magnetic field in the transverse and an alternating magnetic field in the circumferential. The influences of the field strength are discussed. Calculations predict that the magnetoelectric voltage coefficient peaks at resonant frequency of 67.9 kHz. The measured magnetoelectric voltage coefficient peaked at 68 kHz with 1.88 V/cm·Oe. A linear relationship is observed between the magnetoelectric voltage and the alternating field strength under a static field of 340 Oe. This property makes the close-looped sandwich structure a good candidate in current transfer transducer device.
Cu metallization has been widely applied in back-end-of-line (BEOL) of integrated circuit fabrication, as well as in advanced packaging such as 3-D interconnects and through silicon via (TSV). As the device feature size further shrinks, copper diffusion barrier layers with high conductivity, good thermal stability and low Cu diffusion coefficient are to be developed. In this presentation, amorphous metal alloy films of Ta-transition metal (TM = Ni, Cr, Ti) are investigated as a potential copper diffusion barrier. All Ta-TM films deposited on Si showed lower resistivity compared to the conventional Ta nitride barrier films. Ta-Ni films containing up to 86 wt% Ta were found to have as-deposited amorphous phase. Ta-Cr films also contained glassy phase in all studied composition range. However, crystalline phase was observed in the as-deposited Ta-Ti films but the film went through amorphourization during heating. The glassy Ta-Ni thin films showed high stability up to 800°C. Beyond this temperature, crystallization of Ta, Ni$_3$Si$_2$, Ta$_2$O$_5$ and Ta$_5$Si$_3$ were detected. As-deposited glassy Ta-Cr also maintained the amorphous phase up to 800°C, with Ta$_2$O$_5$ and Ta crystalline peak observed. For Ta-Ti films, a solid phase amorphourization was observed when films were annealed at 600°C. The amorphous phase was stable up to 800°C, with Ta$_x$Ti$_{1-x}$O$_2$ crystalline phase has appeared. Therefore it is concluded that Ta-Cr and Ta-Ni has higher glass forming ability and higher thermal stability compared to Ta-Ti films. Copper diffusion barrier performance of Ta-TM films were studied on Cu/Ta-TM/Si stack at different temperatures, ranging from 600 to 800°C. For Cu/Ta-Ti/Si, Solid phase amorphourization of Ta-Ti at 600°C was observed. No Cu$_3$Si peaks were observed for all samples until 700°C. XRD study showed that at 700°C, fast reaction between Cu and Si was observed in Ta-Cr and Ta-Ti barriers, while very low Cu$_3$Si peak could be observed in Ta-Ni barrier. TEM observation showed that Ta-Ti films lost continuity while Ta-Cr and Ta-Ni still maintained integrity at 700°C. The study finds that the Ta-TM binary metallic thin films can be applied as an effective copper diffusion barrier, with low electrical resistivity, high thermal stability and good copper diffusion retardation performance. Among the three systems studied, Ta-Ni barrier is the best, followed by Ta-Cr and Ta-Ti.
