Topical Symposia
Room On Demand - Session TS5

Thin Films on Polymer Substrates: Flexible Electronics and Beyond

TS5-1 Conversion of Aluminium Oxide Coated Films for Food Packaging Applications – From a Single Layer Material to the Finished Pouch, *C. Struller,* Bobst Manchester Ltd., UK; ***Peter Kelly (peter.kelly@mmu.ac.uk)***, Manchester Metropolitan University, UK; *N. Copeland,* Bobst Manchester Ltd, UK

Transparent barrier films based on vacuum deposited aluminium oxide (AlO_x) layers are continuing to create large interest in the market with regards to their use as food and healthcare packaging materials. Nevertheless, their post-metalliser conversion to the final packaging material still presents challenges to current AlO_x producers and the wider converting industry. In this work, AlO_x coated PET films have been developed and then converted in long duration industrial-scale trials via topcoating, printing, lamination and finally pouch making. Throughout this process, each conversion step has been investigated for its effects on the barrier performance. It was found that the printing processes, especially, induce significant damage to the ceramic barrier layer. However, by the use of a protective topcoat prior to any conversion step, the barrier properties of the AlO_x coated film were preserved, or could even be significantly enhanced, depending on the topcoat material. Furthermore, for a barrier topcoat, remarkable stretch- and flex-durability properties were achieved in the final laminate.

TS5-2 Functionalised Copper Nanoparticle Catalysts for Electroless Copper Plating on Textiles, ***Golnaz Taghavi Pourian Azar (ac8637@coventry.ac.uk)***, *A. Cobley,* Coventry University, UK

The MATUROLIFE project utilises two disciplines of materials science and design to meet the needs of older adults to lead independent lives through design-driven Assistive Technology (AT). Metallised conductive textiles are potentially an enabling technology for AT allowing better and more discreet integration of electronics into clothing, footwear, and furniture.

Electroless copper plating can be regarded as an enabling technology for electronic textiles, due to the uniform deposition with consistent thickness, simplicity, and relatively low cost. This procedure is a useful approach to produce electrically and thermally conductive fabrics that are flexible to be utilised as smart textiles. However, the choice of catalyst is crucial to activate the surface and generate nucleation sites for the copper ions to deposit on. The most widely used catalyst is a palladium/tin colloid, however, the use of palladium makes the process expensive. Therefore, alternative and inexpensive metals such as silver and copper have been recently investigated to catalyse the electroless copper plating reactions.

In this study, different catalysts based on Cu nanoparticles (functionalised by various organic molecules) have been utilised for electroless copper plating of textiles. The catalysts were characterised using Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), and X-ray Photoelectron Spectroscopy (XPS). The efficacy of different catalysts was determined by characterising electroless copper-plated textiles in terms of mass gain (after plating), the coatings coverage, and deposits morphology using Scanning Electron Microscopy (SEM). In addition, the sheet resistance of the plated textiles was measured using a four-point probe.

It was found that the degree of coverage of fibres by copper coatings and the resulted conductivities are strongly dependent on the applied catalyst. The results revealed the important role of functionalising molecules on the performance of Cu nanoparticles as a catalyst. Using the best-performing organic molecule in functionalisation of Cu nanoparticle catalyst resulted in coatings with complete coverage and consequently high electrical conductivity being favourably comparable to the coatings catalysed with a Pd catalyst.

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TS5-3 Low-temperature Plasma Enhanced Atomic Layer Deposition of ZnO and Al_2O_3 Thin Films for Applications in Flexible Electronic Devices, ***Jhonathan Castillo (jhonathan.castillo@uabc.edu.mx)***, Universidad Autónoma de Baja California , Colombia; *N. Nedev,* Universidad Autónoma de Baja California , Bulgaria; *B. Valdez,* Universidad Autónoma de Baja California, Mexico; *N. Hernandez,* Instituto Politécnico Nacional (IPN), Mexico; *E. Martinez,* Centro de Investigación en Materiales Avanzados (CIMAV) , Mexico; *M. Curiel,* Universidad Autónoma de Baja California , Mexico; *M. Mendivil, M. Martinez,* Centro de Investigación en Materiales Avanzados (CIMAV), Mexico

Thin films of zinc oxide (ZnO) and aluminum oxide (Al_2O_3) were grown by plasma-enhanced atomic layer deposition (PE-ALD) using O_2 and H_2O plasma at 70 °C. An optimization of deposition parameters was performed in order to obtain atomically saturated layers. The films were grown on ITO/Glass, quartz, p-type silicon and polyethylene terephthalate (PET) substrates. X-ray photoelectron spectroscopy (XPS) revealed a high purity of the obtained films. The optical constants and thicknesses of the grown layers were determined by spectroscopic ellipsometry, while the roughness was measured by atomic force microscopy. High transmittance, above ~90%, was measured by UV-Vis spectroscopy. Electrical characterization was carried out using Keythley 4200 Semiconductor Characterization System. ZnO and Al_2O_3 films were used to fabricate transparent thin film transistors (TFT) on ITO/Glass substrates by means of photolithography.The thickness of the ZnO (n-type semiconductor) was 60 nm, while the thickness of the gate oxide (Al_2O_3) was varied (25, 50 and 100 nm). Aluminum with thickness of 200 nm was used as a gate electrode and source and drain contacts.

The films obtained showed excellent optical, structural, compositional, morphological and electrical properties, what make them promising candidate for electronic and optoelectronic applications, which require low temperature processes.

Keywords: PE-ALD, ZnO, Al_2O_3, low temperature, TFTs, thin films, flexible electronic

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TS5-4 Roll-to-Roll Reactive Ion Etching of Nanoscale Features in Si for Next Generation Flexible Electronics, ***Ziam Ghaznavi (z.ghaznavi@eandr.com)***, Emerson and Renwick Ltd., USA; *N. Butcher, J. Crowther,* Emerson and Renwick Ltd., UK

Roll-to-Roll (R2R) processing has garnered significant research interest from industry in recent years due to its potential ability to simultaneously address throughput and cost requirements for next generation flexible electronics and the Internet of Things (IoT). However, a complete ecosystem of R2R tools including patterning, deposition, and etch is needed in order to facilitate the transition of device fabrication from wafer-scale to the continuous regime. Many prospective applications also require nanoscale control and repeatability for yield management which necessitates thorough characterization of each process step and an in-depth understanding of the underlying physics of these R2R tools compared to their wafer-scale counterparts particularly during pattern transfer i.e. etching. This work demonstrates progress towards process development and control on an exemplary semiconductor device fabrication scheme utilizing Emerson & Renwick's Genesis R2R platform. Specifically, we successfully demonstrate etching nanoimprinted patterns of nanopillars into Si in a continuous R2R fashion with submicron resolution. Process verification details include quantifying etch uniformity, directionality and material selectivity at varying web speeds. Furthermore, we discuss the systematic characterization of the constituent processes and equipment by intelligent Design of Experiment (DOE) allowing for process parameter tuning to meet desired etch targets.

TS5-5 HiPIMS Metallization of Polymers: Titanium on PEEK, ***Aarati Chacko (aarati.chacko@empa.ch)***, *K. Thorwarth, R. Crockett, U. Müller, H. Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Metallized polymers are becoming a prevalent part of our world, be it in electronic, medical or transport applications, and the performance requirements for these metal-polymer systems are becoming more demanding. Meeting these requirements means gaining a better understanding of plasma-polymer and metal-polymer interactions, both of which can occur in coating processes. High Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor deposition method characterized by a large fraction of ionized metal species in the coating discharge, which allows for a high level of control over film-forming species. This makes

HiPIMS a method of choice to study and tailor the substrate-film interphase region responsible for 'good' and long-lived thin film adhesion. However, prior to HiPIMS metallization, the polymer must be 'activated' such as to raise its surface energy.

In this work, we evaluate the chemistry of a polymer surface before and after plasma activation using XPS, ToF-SIMS and ATR-FTIR. We then relate this to HiPIMS-metallized surfaces and interfaces using the same techniques. The test metal-polymer system for this study is titanium on Polyetheretherketone (PEEK), a system that has shown exemplary adhesion in a former study.

TS5-6 Fragmentation of ALD-PVD Multilayers on Flexible Substrates in Uniaxial and Biaxial Tension: Insights from in situ SEM and Synchrotron Diffraction Experiments, ***Barbara Putz (barbara.putz@empa.ch)***, *T. Edwards, T. Xie, E. Huszar, L. Pethö,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Kreiml,* Montanuniversität Leoben, Department of Material Physics, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Thiaudiere,* Synchrotron SOLEIL, France*; D. Faurie,* LSPM-CNRS, Université Paris13, France*; P. Renault,* Université de Poitiers, France*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Brittle layers are often dominating the deformation behavior of flexible thin film multilayer structures, where the modulation period ($t_{brittle} + t_{ductile}$) as well as the modulation ratio ($t_{brittle}/t_{ductile}$) influence the extent of embrittlement [1].

In this work, a unique combination of atomic layer (ALD) and physical vapor deposition (PVD) is used to fabricate model multilayers of Al and Al2O3 and study fundamental deformation mechanisms in brittle/ductile multilayers on flexible polymer substrates (Polyimide, 50 µm, Upilex-S®). The ability of operating the ALD/PVD process without breaking vacuum opens up a wide range of otherwise unachievable modulation and thickness ratios. For Al2O3 layers thickness control with precision down to 0.1 nm can be achieved. The investigated individual layer thicknesses are 50nm for Al (PVD) and 0.1 nm – 10 nm for Al2O3 (ALD) layers. Constant oxide thicknesses (50/2/50/2…) and cross-sectional thickness variations (50/1/50/3…) are used to determine crack onset and propagation as a function of oxide layer thickness during *in situ* uni- and biaxial tensile experiments. Uniaxial fragmentation is studied *in situ* with scanning election microscopy (SEM) and focused ion beam cross-sectioning. This *in situ* approach avoids crack closure due to relaxation of the polymer substrate after unloading. Biaxial tensile experiments, performed at the Synchrotron Soleil (Paris, France), reveal the evolution of Al film stresses as a function of applied strain from X-ray diffraction and $\sin^2\psi$ analysis. Digital image correlation is used to measure true strains on the thin film surfaces. All multilayer structures have good adhesion between individual layers as well as to the polymer substrate. Grain growth of Al is limited by the Al2O3 layers, allowing for easy discrimination of individual Al layers. The Al2O3 layers show increasing stretchability with decreasing film thickness, as a result of being extremely well defined and practically defect free. In biaxial tension, fracture of 8nm Al2O3 at 2.2% strain induces through thickness cracking. Crack onset correlates to a relaxation of the Al film stresses. In contrast, samples with 2nm oxide layers do not exhibit a pronounced crack pattern or stress relaxation within the tested strain regime.

The possibility to manipulate Al grain sizes by ultrathin ALD layers and the observed deformation behavior of the multilayers highlights the potential of the combined deposition technique for designing flexible thin film systems with improved strength and damage tolerance.

[1] K. Wu, J.Y. Zhang, J. Li, Y.Q. Wang, G. Liu, J. Sun, Acta Mater. 100 (2015) 344–358.

TS5-7 Optically Transparent Bacterial Nanocellulose Composites and Fibroin Substrates for Flexible Organic Devices, ***Marco Cremona (cremona@fis.puc-rio.br)***, Pontifícia Universidade Católica do Rio de Janeiro, Brazil*; H. Barud,* Universidade de Araraquara, Brazil*; R. Carvalho,* Pontifícia Universidade Católica do Rio de Janeiro, Brazil*; A. Cebrian,* UNESP, Brazil*; A. Barreto,* PUC-Rio, Brazil*; F. Maturi,* UNESP, Brazil*; R. Silva,* Chalmers University Technology, Sweden*; C. Legnani,* Universidade Federal de Juiz de Fora, Brazil*; S. Ribeiro,* UNESP, Brazil

Cellulose is the most abundant organic material on Earth and an important resource for eco sustainable platform for flexible electronics. Bacterial cellulose (BC) is a good biopolymer choice for applications in the medical field and already reported as substrates for organic devices as organic light emitting diodes (OLEDs). BC can be produced by some species of bacteria as *Gluconacetobacter xylinus* and have been demonstrating a quite promising material due to its high degree of polymerization and higher tensile strength (200-300MPa) and Young's modulus (up to 80GPa). BC substrates are in general semitransparent in the visible region due to the presence of air in the interstices between the cellulosic nanofibers. Efforts to solve this disadvantage have been reported in the literature, with the use of several polymers to fill BC interstices. However, such methods are not always economically feasible, scalable, simple, fast and with chemically green synthetic route. In this work, a polymer from recyclable source, Expanded Polystyrene (EPS), dissolved in a green solvent, d-limonene, was used as biocompatible and conformable substrates for highly efficient green OLEDs. Polystyrene is a polymer having a refractive index (h = 1.5916) close to that of the BC and can be used to fill the interstices between the cellulosic nanofibers increasing the optical transmission. Visible light transmission improves to up 88%, instead of 40% previously achieved by pristine BC. BC-PS substrates were produced by airbrush technique deposition of PS on BC pristine films. These multifunctional composite substrates were successively covered with silicon dioxide (SiO_2) and Indium Tin Oxide (ITO) thin films to be used as conductive substrates. Finally, transparent BC-PS was evaluated as conformable substrate for OLED application. The biocompatible and conformable green OLEDs produced presented current efficiency up to 5cd/A and power density around 2.8mW/cm^2, and are promising as light source for light therapy such as PDT and burning wound healing. Additionally, organic field emission transistors (OFETs) using polyurethane as dielectrics, P3HT as organic semiconductor and Au as contacts and Al as gate were fabricated onto transparent fibroin substrate. The devices retained their properties even under high curvature stresses, presenting maximum values for mobility of 1.8×10^{-2}cm^2/Vs, threshold voltages of -7.6V and low leakage current up to 50V.

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