

SYMPOSIUM V

Materials Development for Direct Write Technologies

April 24 – 26, 2000

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* Invited paper

SESSION VI: OVERVIEW OF DIRECT WRITE

Chair: Douglas B. Chrisey
Monday Morning, April 24, 2000
Salon 12 (Marriott)

8:30 AM *V1.1

THE POTENTIAL OF DIRECT-WRITE TECHNOLOGIES.

William L. Warren, DARPA, Arlington, VA.

The goal of the DARRA MICE (mesoscopic integrated conformal electronics) program is to demonstrate the rapid prototyping and manufacturing of miniaturized and rugged mesoscopic electronics on any surface through the 3-dimensional integration of passive components (resistors, capacitors, inductors high gain antennae, and interconnects) and active components (batteries, etc.) using a direct-write approach. Mesoscopic electronic devices are defined as electronic devices that straddle the size range between conventional microelectronics (sub-micron-range) and traditional surface mount components (10 mm-range). The MICE direct-write machine goal is to develop a system capable of rapid manufacturing that can deposit a wide variety of materials (conductors, insulators, ferrites, ruthenates, polymers, etc.) for customized, robust, electronic devices in a 3D fashion at low-substrate temperatures in a conformal manner on virtually any substrate (paper, plastic, ceramics, etc.). The ultimate advantage of the MICE approach is that it integrates many functions into one conformal electronic system including advanced batteries, advanced electronics, and functional devices. The talk will provide a brief discussion of the various direct-write technologies being funded by DARPA as well as the many differing applications that become significantly enhanced or enabled via the MICE technology. Such applications include: miniature passive components for microsatellites, munitions, toys, and wireless communications (cell phones, GPS, etc.), embedded sensors for conditioned based maintenance and for the medical industry (e.g., sensors for pressure, temperature, voltage, humidity, etc.), as well as for tissue engineering to name a few. The ability to direct-write power offers many system advantages from higher battery specific energy densities to lower overall system weight. Many advantages are realized because the power is an integral part of the structure, on which the electronic systems will be used; there will be no need for a traditional printed wiring board. Thus, machines and electronics can become one for systems optimization.

9:00 AM V1.2

DIRECT FOCUSED ION BEAM WRITING OF PRINTHEADS FOR PATTERN TRANSFER UTILIZING MICROCONTACT PRINTING.

David M. Longo and Robert Hull, University of Virginia, Department of Materials Science & Engineering, Charlottesville, VA.

We describe how focused ion beam (FIB) direct write technology may be combined with microcontact printing (μ CP) and other pattern transfer techniques to enable nanoscale fabrication of complex patterns over both curved and planar surfaces. Nanoscale printheads are fabricated by direct sputtering or deposition (Pt or SiO₂) in the FIB. These printheads are capable of transferring 100 nm features over fields of view up to 1 mm², onto planar and curved surfaces. The FIB used in this work is an FEI 200, utilizing a Ga⁺ or In⁺ liquid metal source, with ion energies of 30 keV, a minimum spot size \sim 10 nm and an ion current density \sim 10 A/cm². Feature sizes of order 0.1 μ m may be fabricated by both milling and deposition. The field of view is 1 mm². Calibrated drift rates are as low as 1.5 nm/min. The depth of focus is very high compared to optical or electron lithography - measured to be of order 200 μ m in our system. Utilizing these capabilities, we have been able to fabricate patterns in the FIB for transfer to target substrates via μ CP with polydimethylsiloxane (PDMS) replicas of our original patterns. These patterns can be fabricated on planar or curved printheads, and then transferred to planar or curved substrates. We are also investigating the concept of "programmable" printheads by fabrication of individually addressable printhead arrays, coupled with selective desorption of a relevant transfer medium (e.g. hexadecanethiol self-assembling monolayers) by heating or by application of an electric field. These addressable printhead arrays have been fabricated in the FIB by a combination of FIB milling, μ CP, and FIB deposition of both Pt and SiO₂. By co-depositing Pt and SiO₂, we are exploring the feasibility of "tunable" resistance in our active printing elements.

9:15 AM *V1.3

THERMAL SPRAY TECHNIQUES FOR PRODUCING MULTI-LAYER ELECTRONIC CIRCUITS AND SENSORS.

Herbert Herman, Sanjay Sampath, Richard Gambino, Ashish Patel and Andrew Dent, SUNY Stony Brook, Dept of Materials Science and Center for Thermal Spray Research, Stony Brook, NY; Ellen Tormey, Sarnoff Corp, Princeton, NJ.

Thermal spray direct-write techniques are being employed to cost-effectively produce mesoscopic-sized components for integrated electronic circuits, which will be used in wide ranging applications

(e.g., sensor elements, rapidly-produced prototype circuits). The spray devices employed here are novel, but are essentially based on variations of reasonably well established thermal spray methods: e.g., High-Velocity Oxy-Fuel, Plasma Spray, and Solid State Supersonic Spray Deposition. To date, employing spray focussed-beams and collimation systems, we have spray-formed fine silver conductor lines having two-times bulk resistivity, capacitive components based on barium titanate with as-sprayed dielectric constants of over 80, ferrites with saturation magnetizations of 4000 gauss, coercivities of 50 Oe with resistivities of 78 ohm-cm, and resistors having sheet resistances in the range of 50 Ohm/sq. to 1kOhm/sq. Hybrid thermal spray systems have allowed us to fabricate a high frequency inductance circuit. Relative to its benefits for the production of a wide range of electronic circuits, thermal spray is a unique means for processing high performance materials into functional forms. The features of thermal spray directly relevant to electronic circuits include: Wide availability of sprayable materials (conductors, resistors, dielectrics, capacitors, magnetic components); Multiple materials can be simultaneously processed to achieve composites and graded deposits; High speed of deposition, relative to competitive methods; Post-treatment is generally not required; Fully dense deposits are achievable; Heat input to the substrate can be minimized; Amenable to both process control and automation for conformal deposition; Fine spray-print achievable; Thicknesses currently can range from 5 micrometers to bulk forms. A discussion will be presented of challenges and promising directions in this program. This research is supported by DARPA/ONR through Grant: N00014-98-C-0182.

9:45 AM V1.4

CHARGED MOLTEN METAL DROPLET DEPOSITION AS A DIRECT WRITE TECHNOLOGY. Melissa Orme, Qingbin Liu, Jun Zhu, Robert Smith, University of California, Irvine, Department of Mechanical and Aerospace Engineering, Irvine, CA.

The formation and control of highly uniform charged molten metal droplets from capillary stream break-up has recently attracted significant industrial and academic interest for applications requiring high-speed and high-precision deposition of molten metal droplets such as direct write technologies. Exploitation of the high droplet production rates intrinsic to the phenomenon of capillary stream break-up, and the unparalleled uniformity of droplet sizes and speeds attained with proper applied forcing to the capillary stream make many new applications related to the manufacture of electronic packages, circuit board printing and rapid prototyping of structural components feasible. Recent research results have increased the stream stability with novel acoustic excitation methods, and enable ultra-precise charged droplet deflection. Unlike other modes of droplet generation such as Drop-on-Demand, droplets can be generated at rates typically on the order of 20,000 drops per second, (depending on droplet diameter and stream speed) and can be electrostatically charged and deflected onto a substrate with a measured accuracy of \pm 12.5 μ m. Droplets are charged on a drop-to-drop basis, enabling the direct writing of fine details at high speed. Issues relevant to high quality droplet writing include: (1) those that affect the geometric resolution of the printed artifact, and (2) those that affect the microstructure and mechanical properties of the fabricated artifact. The factors that affect the geometric fidelity of the component include: attainment of desired electrostatic charge, mutual electrostatic interactions between charged drops, and aerodynamic effects during droplet flight to the substrate. Factors affecting microstructure and material properties are: solidification rate, phase change for remelting the previously deposited and solidified material, and the elimination of oxygen in the printing environment or oxides in the melt. The above issues are investigated in a systematic manner in order to understand their relative importance in the emerging direct write technology.

10:15 AM *V1.5

MICROPEN DIRECT WRITE FABRICATION OF INTEGRATED ELECTROCERAMIC DEVICES. Duane Dimos, Paul G. Clem, Nelson S. Bell, Terry J. Garino, Pin Yang, Mark A. Rodriguez, Sandia National Laboratories, Albuquerque, NM.

The desire to have smaller electronic packages and components with greater functionality and enhanced reliability requires the ability to integrate electronic ceramics (and metals) in complex 3-D architectures. To address this need, we are developing a direct-write fabrication approach that reduces turnaround time and improves design flexibility. The direct-write approach uses a commercial Micropen, which is a computer automated system for precision deposition of slurries. The Micropen is used to build up hybrid components layer by layer or by combining several materials in a single layer. One critical issue for direct-write fabrication of these integrated components is the relationship between slurry rheology and print topology. We have characterized this relationship for commercial pastes and custom slurries. Since differential shrinkage can lead to

defects in these multilayer structures, we have also characterized the sintering behavior of individual layers, in constrained and unconstrained situations, and bilayers using two customized techniques. In-situ techniques for evaluating reactivity between various thick films are also being developed and used to assess compatibility. In addition, this direct-write approach is being applied to fabricating materials with reduced processing temperatures for integration with organic substrates. Material compatibility as well as the design and performance of devices will be discussed.

10:45 AM V1.6

MANUFACTURE OF MICROELECTRONIC CIRCUITRY BY DROP-ON-DEMAND DISPENSING OF NANO-PARTICLE LIQUID SUSPENSIONS. John B. Szczech, Constantine M. Megaridis, University of Illinois at Chicago, Dept of Mechanical Engineering, Chicago, IL; Dan Gamota, Jie Zhang, Motorola Advanced Technology Center, Schaumburg, IL.

In the area of Imaging Science, Drop-On-Demand (DOD) Ink Jet Technology has proven to be an efficient means of depositing pigmented inks on a variety of media. The ability for DOD Technology to repeatedly generate high-resolution patterns at relatively rapid rates makes it a potential candidate for the direct write of circuitry and electronic devices. Solder Jetting Technology has demonstrated the effectiveness of DOD for the fabrication of vertical interconnects for Chip Packaging applications.

An emerging deposition technology currently under investigation at the Droplet and Particle Technology Laboratory of the University of Illinois at Chicago and Motorola replaces solder with a nano-particle suspension. The suspension consists of silver or gold particulates of 1-10 nanometers in size that are homogeneously suspended in an organic carrier. A piezo-electric droplet generator driven by a bipolar voltage signal is used to dispense 50-70 micron diameter droplets traveling at 1-3 m/s before impacting a compliant substrate. The substrate is subsequently processed at 300C for 15 minutes to allow for annealing of the nano-particles and evaporation of the carrier, thereby yielding a finished circuit product.

Recent attempts in this program to fabricate circuit interconnection and transmission lines have proven successful. Circuitry created using this technique exhibited features as fine as 100-125 microns wide and 1-3 microns thick. The circuitry performed well during environmental conditioning and reliability studies. However, repeatability of the results relies heavily on the generation of steady, satellite-free droplets. In an effort to generate droplets of consistent parameters, it is essential to develop a strong fundamental understanding for the correlation between device excitation parameters and fluid properties, and to appreciate the microrheological behavior of the conductive ink as it flows through the droplet generator.

11:00 AM V1.7

ION BEAM INDUCED CHEMICAL VAPOR DEPOSITION OF DIELECTRIC MATERIALS. Heinz D. Wanzenboeck, Alois Lugstein, Helmut Langfischer, Emmerich Bertagnolli, Vienna University of Technology, Institute for Solid State Electronics, Semiconductor Technology, Vienna, AUSTRIA; Martin Gritsch, Herbert Hutter, Vienna University of Technology, Institute for Analytical Chemistry, Vienna, AUSTRIA.

Materials providing a deposition technology applicable in the sub-m range are the key factor for development of microelectronic devices. Especially dielectric thin films are essential materials for providing reliable electric insulation. A focused ion beam tool allowing locally confined chemical vapor deposition has been applied to direct-write tailor-made microstructures of siliconoxide as applied for the modification and repair of microelectronic circuits. However, state-of-the-art procedures provide insufficient dielectrics with high leakage currents and low breakdown voltage. The detailed investigation of the deposition mechanisms should lead to significantly improved dielectric material properties. Using siloxane and oxygen as volatile precursor introduced via a nozzle system siliconoxide was deposited at ambient temperatures on various materials such as Si, GaAs, or metals. The deposition process was initiated by a focused Ga+ beam at acceleration voltages between 5-50 kV with a diameter down to 5 nm. The control of beam and gas system allowed to independently influence either the adsorption or the subsequent surface reaction. Ion beam induced depositions in a capacitor design performed as elementary electronic test vehicles for a systematic investigation of conductivity and breakdown voltage. The chemical composition of the layers was investigated by secondary ion mass spectroscopy (SIMS) and revealed effects of atomic mixing from both, the substrate and the beam. The variation of process parameters such as ion energy and dose, scan time and delay time lead to a better understanding of the mechanism. The delay time between scans was found critical for the re-adsorption of precursor compounds. The composition of the precursor gas mixture is of significant influence on insulating properties. The optimum process was obtained with a moderate excess of oxygen in the gas phase. The impact of thermal

post-processing was evaluated by electrical testing. The results demonstrate that optimized FIB-induced deposition of dielectrics offers a new window for in-situ post-processing of integrated circuits.

11:15 AM *V1.8

PULSED UV LASER APPROACHES TO DIRECT WRITE PROCESSING. David P. Taylor, Bill Hansen, Pete Fuqua, Meg Abraham and Henry Helvajian The Aerospace Corporation, Los Angeles, CA.

Laser based direct write processing has many advantages for rapid prototyping and specific fabrication applications. A disadvantage of this approach is that it does not lead to very efficient deposition or removal of significant volumes of material. This is a particular problem for the fabrication of true 3D pieces required by certain devices. Our efforts to develop efficient processing techniques include both laser seed templates for electroless plating and laser exposed etchable glass ceramics. In both of these examples, the direct write process employs a pulsed UV laser to make an electronic transition in a non-silicon material that is exploited by subsequent batch processing. This "non-thermal" approach can be contrasted to thermal direct write processing which uses the laser to deposit heat at a particular point: either to accelerate a reaction rate or to move material using ablation. Some of our recent work in the area of 'non-thermal' direct write laser processing will be presented.

11:45 AM V1.9

COMMERCIAL APPLICATIONS AND REVIEW FOR DIRECT WRITE TECHNOLOGIES. Kenneth H. Church, CMS Technetronics Inc, Stillwater, OK.

Direct write in the past has generated the excitement of possibly replacing photoresist for all electronic applications. Removing the mask would substantially reduce the number of steps required to produce electronic circuits. A reduction in steps represented time and dollar savings. The advantage of being able to direct write a manufacturable device would also save time and money in the design process as well. With all of the obvious advantages, it seemed inevitable that research dollars would continue to mount and thus overcome the obstacles preventing this technology from becoming more than a novel technique used in laboratories. As Moore's law began to settle in, so did photoresist and direct write was little more than a novelty. That was then, and this is now. Developers have come to terms with the true value direct write can supply to the manufacturers and design engineers. Techniques such as Focused Ion Beam (FIB), Laser Chemical Vapor Deposition (LCVD), ink jetting and ink penning have found real applications that are making a difference in industry. A summary will be presented describing the various direct write techniques, their current applications and the possible or probable applications.

SESSION V2: MATERIALS DEVELOPMENT

Chair: Daniel R. Gamota
Monday Afternoon, April 24, 2000
Salon 12 (Marriott)

1:30 PM *V2.1

THICK FILM MATERIALS FOR DIRECT WRITE ELECTRONICS. Paolina Atanassova, Mark J. Hampden-Smith, Toivo Kodas, Klaus Kunze, Superior MicroPowders, LLC, Hawkins NE, Albuquerque, NM.

Direct write processes for electronic materials can rely on either volatile or involatile reactants delivered to surfaces through a variety of approaches. Here we discuss strategies exploiting involatile precursors for the generation of features on surfaces. General materials approaches for deposition of conductor, resistor, capacitor and inductor materials on a variety of substrates will be presented. Approaches include both low-temperature conventional heating and laser processing of molecular precursors and powders.

2:00 PM V2.2

DEPOSITION OF CERAMIC MATERIALS USING POWDER AND PRECURSOR VEHICLE VIA DIRECT WRITE PROCESSING. Philip D. Rack, Rochester Institute of Technology, Dept. of Microelectronics Engineering, Rochester, NY; James M. Fitz-Gerald, Naval Research Laboratory, Washington, DC; A.C. Geiculescu, H.J. Rack, Clemson University, Dept. of Ceramic and Materials Engineering, Clemson, SC; A. Piqué, R.C.Y. Auyeung, S. Lakeou, D.B. Chrisey, Naval Research Laboratory, Washington, DC.

Ceramic materials are critical components for electronic and luminescent devices. At NRL, we have developed a method to direct write ceramic materials with feature sizes $\leq 10\mu\text{m}$ which have both electronic and display applications. This technique termed Matrix Assisted Pulsed Laser Evaporation Direct Write (MAPLE DW) uses a

high energy focussed photon source in combination with a ribbon to fabricate materials onto a range of substrates at room temperature without material degradation. Three different cases will be discussed with respect to ribbon manufacturing in terms of powder/precursor combinations. In addition, the use of precursor materials as transport vehicles to aid in the bulk adhesion and density properties will also be presented. For these experiments a pulsed excimer laser ($\lambda = 248 \text{ nm}$) was used, focused down to average spot sizes ranging from 10 - 200 μm with fluences ranging from 0.1 to 1.5 J/cm^2 at repetition rates between 1-50 Hz. All depositions were performed at room temperature and atmospheric pressure. In-situ and ex-situ annealing of the transferred materials was performed by both pulsed ND:YAG laser and conventional furnace heat treatments at temperatures ranging from 200-300°C. Laser transfer results of dielectrics, and luminescent materials will be presented. Characterization of ribbon and transferred materials were performed by SEM, XRD, PL, CL, and 3-D surface profilometry.

2:15 PM V2.3

THICK FILM HIGH K DIELECTRICS FOR DIRECT WRITE ELECTRONICS. Paolina Atanassova, Mark J. Hampden-Smith, Toivo Kodas, Klaus Kunze, Superior MicroPowders LLC, Albuquerque, NM.

The proper selection of precursors and the design of solution or paste formulations for direct write high k ceramic materials are equally important in achieving desired dielectric properties like low loss, high k, low CTE, and dielectric strength at various frequencies. Useful approaches for formulation of suitable starting materials and structural characterization of deposited test structures will be presented and related to the different uses of these materials in direct write applications. In this respect, another emphasis will be on the discussion of selecting functional components that will lead to patterns formed by low temperature conversion on different substrates.

2:30 PM V2.4

ROLE OF POWDER PRODUCTION ROUTES IN DIRECT WRITE APPLICATIONS. M.B. Arun Ranade, Particle Technology, Inc., Beltsville, MD.

A variety of production techniques are available for many materials in the direct write applications. Single metals and alloys are prepared by vapor and spray reactors as well as by precipitation techniques. Single and multicomponent oxides such as ferrites are also possible from these techniques in the nanoscale to micrometer size ranges. In this presentation, experience with the use of alternate techniques for production of metals and ferrites of widely differing sizes will be discussed with a focus on their application in direct write processes with comparison of properties such as crystallinity and morphology.

3:00 PM V2.5

THICK FILM CONDUCTOR MATERIALS FOR DIRECT WRITE ELECTRONICS. Paolina Atanassova, Mark J. Hampden-Smith, Toivo Kodas, Klaus Kunze, Superior MicroPowders, LLC, Albuquerque, NM.

The fast processing rates, low conversion temperatures and low densification temperatures required for direct write processes of electronic materials impose unique requirements for the materials used. Similar to conventional thick film processing, direct write deposition of thick film conductor materials requires a combination of conductor powder, a vehicle suitable for the particular deposition method and additives that ensure adhesion and/or proper fluid rheology. Materials approaches for the choice of powder, precursors and vehicle characteristics that address the fast processing and low temperature conversion requirements of direct write processes are discussed.

3:15 PM V2.6

MATERIAL SYSTEMS USED BY MICRO DISPENSING AND INK JETTING TECHNOLOGIES. Jie Zhang, Irina Shmagin and Daniel Gamota Motorola Advanced Technology Center, Schaumburg, IL.

In today's electronic industry, manufacturers are continuously demanding to improve capital utilization, develop flexible manufacturing process, reduce changeover time and improve yield and throughput. Interests in rapid prototyping and 3-D fabrication capabilities are rapidly increasing, and a number of candidate direct writing technologies are in development to meet these demands. This study surveys advanced deposition technologies and material systems for potential low temperature reel-to-reel high volume manufacturing on low cost substrates. Characterization results of fabricated discrete and RF devices using commercially available micro dispensing and ink jet systems will be discussed. Material rheological properties, deposition process characterization, deposition repeatability, fabricated device reliability and electrical performance will be presented. The test vehicles are PTF resistors and capacitors, transmission lines, open and short series stub filters, and

half-wavelength resonators. The material/substrate compatibility will be demonstrated through environmental conditioning of the test vehicles. In addition, a cost estimation for using micro dispensing technologies is conducted to compare it to current manufacturing technologies.

3:30 PM V2.7

DIGITAL PRINTING OF LUMINESCENT MATERIALS. Mark J. Hampden-Smith, Toivo T. Kodas, Superior MicroPowders, Albuquerque, NM.

Digital printing of luminescent materials has value in a wide number of markets including medical markets (utilizing precise delivery), display markets (where direct deposition through an additive process can reduce processing steps) and security markets (where CAD/CAM compatibility make frequent design changes feasible). Superior MicroPowders produces spherical morphology, suspendable luminescent powders that are uniquely suited to digital printing, especially ink-jet printing. This presentation will describe the advantages of using micron-sized, spherical morphology, controlled particle size distribution inorganic phosphor powders such as $\text{Y}_2\text{O}_3\text{:Eu}$, $(\text{Y,Gd})\text{BO}_3\text{:Eu}$, $\text{Zn}_2\text{SiO}_4\text{:Mn}$ and $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ for use in display and lighting applications. The mechanisms of solution stabilization and the results of ink-jet printing these and other luminescent powders in commercial piezoceramic ink-jet printing systems for various market applications will be described.

3:45 PM V2.8

DIRECT WET PRINTING OF POLYMER SOLUTIONS FOR HIGH RESOLUTION LITHOGRAPHY. Scott M. Miller, Anton A. Darhuber, Sandra M. Troian, Princeton University, Dept. of Chemical Engineering; Sigurd Wagner, Princeton University, Dept. of Electrical Engineering, Princeton, NJ.

We have investigated the direct printing of polymer solutions from flat but chemically patterned substrates as a new high-throughput alternative to optical lithography. The chemically defined surface pattern on the substrates (stamps) is achieved by patterning a monolayer of octadecyltrichlorosilane (OTS) on a silicon wafer by deep UV lithography. The Si-C bonds in the exposed regions are subject to photocleavage rendering these areas completely hydrophilic. Aqueous solutions of polymers and oligomers are then deposited on the hydrophilic surface patterns by means of a dip-coating technique. The dependence of this deposition process on the viscosity of the solution and the speed of withdrawal was studied. The liquid patterns are printed onto a target substrate by means of a motion controlled press. In this way, we have successfully printed five micron wide polymer lines onto a silicon wafer. To complement these experimental studies, we have initiated numerical simulations of the stability of liquid droplets residing on a heterogeneously patterned surface before and after transfer to a target surface. Suitable control over the aspect ratios of the surface pattern as well as the liquid surface tension improve the pattern fidelity upon transfer. Methods for the stabilization of the printed polymer pattern on the target surface against subsequent spreading or capillary breakup will be discussed.

4:00 PM V2.9

SOLGEL-DERIVED O3 COMPOSITE MATERIALS FOR DIRECT-WRITE ELECTRONICS APPLICATIONS. Steve Coleman^{1,2}, Robert Parkhill², Robert Taylor² and Edward Knobbe¹.
¹Thin Film and Materials Processing Group, Department of Chemistry, Oklahoma State University, Stillwater, OK, ²CMS Technetronics, Stillwater, OK.

New solgel-derived O3 composite ceramics are presently being developed for direct-write electronics applications. These O3 composite materials are prepared from a mixture of liquid and solid phase constituents, as are conventional pastes used in the preparation of thick film materials for the electronics industry. When compared with conventional paste materials and processes, however, the new O3 composites exhibit several potential advantages including substantially reduced processing temperatures. Sol-gel derived systems have been shown to be compatible with the development of rapid prototyping methods, such as laser densification. Sol-gel chemistry also imparts the potential for greatly enhanced adhesion to a variety of substrates, including ceramics, semiconductors, and plastics. The current status of activities aimed at direct-write sol-gel O-3 composite electronics device components will be described.

4:15 PM V2.10

CONTROLLED THERMAL DEGRADATION IN THE DESIGN OF POLYMERS FOR LITHOGRAPHIC APPLICATIONS. Stefan O. Vansteenkiste, Yves Martelé Etienne H. Schacht, University of Ghent, Dept. Organic Chemistry, Ghent, BELGIUM; Marc Van Damme, Huub van Aert, Joan Vermeersch, Agfa-Gevaert N.V., Mortsel, BELGIUM.

Until recently, pulsed solid-state lasers (i.e. Nd-YAG), did not offer the required pulse energies, within the IR-range (830 or 1034 nm), compared with UV-excimer lasers for micromachining or ablation applications. However, current technological advances have led to the development of a new generation of diode-pumped (DPSS) solid-state lasers that emit sufficient energy outputs to create opportunities for machining, marking or patterning processes. Since the entire output beam from a DPSS laser can be focused to achieve spot sizes of 15-30 μm over large working distances, this technology eliminates the need for photo-masks and allows material modification in a 'direct-write' fashion. Therefore, this process offers excellent opportunities in the design of dry imaging systems (ex. printing plates) which are applicable under daylight conditions. In this study, a synthetic route was devised yielding the *tert*.butyl carbonic anhydrides of 4-carboxystyrene and methacrylic acid. This new class of thermo- and acid-labile *tert*.butyl-protected monomers and corresponding polymers allows a high thermosensitivity while still resulting in a carbonic acid after deprotection, providing a significant polarity change as was monitored by dynamic contact angle measurements. Subsequently, the interaction between polymer substrates, prepared by solvent or spin casting, with I.R.-laser light was evaluated. The influence of a wide range of parameters such as illumination conditions, polymer sensitivity, identification of the degradation products (TGA-GC-MS-analysis) governing the processibility and the applicability of the system, were studied. The morphology of the obtained patterns (resolution, control over edge profiles, surface roughness), was visualized with nanometer resolution by SEM, AFM and profilometry. Finally, the lithographic performance of both materials was evaluated in the presence of diaryliodonium triflate as thermoacid generating species. It was demonstrated that the large polarity change results in a positively working chemically amplified thermoresist system.

4:30 PM V2.11

ELECTRICAL CHARACTERISTICS OF THERMAL SPRAY SILICON COATINGS. S.Y. Tan, R.J. Gambino, R. Goswami, S. Sampath, H. Herman, State Univ of New York at Stony Brook, Dept of Materials Science and Engineering, Stony Brook, NY.

We are investigating the direct spray of silicon for devices. Silicon deposits on monocrystalline silicon substrates were formed employing thermal spray techniques. Silicon powder is injected into a high-energy flame, where the silicon particles are melted and accelerated within the flame directing towards a rotating substrate. Upon impact, the kinetic energy of the molten silicon generates a shock wave, which propagates through the underlying silicon layer, causing a phase transformation to a high pressure form of silicon. The silicon coating is polycrystalline, consisting of several silicon phases, such as Si-I, Si-III, Si-IV, Si-IX, which are the metastable phases retained after depressurization. The polycrystalline silicon coating exhibits a fine dispersion of nanocrystalline grains of the pressure quenched phases, with varying sizes and random orientation. The present work addresses experiment and theory to investigate the electrical characteristics, namely, resistivity and mobility of the polycrystalline silicon coating in the presence of different high pressure silicon phases, varying nanocrystalline grain sizes, grain orientation and grain boundaries. Hall measurements have been performed and show a mobility on the order of 50, about one order of magnitude less than typical values for single crystal silicon. The resistivity value of 1 ohm-cm, when converted into impurity concentration, gives 10^{16} atoms/cm³ of silicon. The sign of the Hall effect indicates P-type doping. The carrier type was confirmed by the sign of the thermoelectric power. Never the less, the coating and P-type single crystal substrate form a rectifying junction at the polycrystalline coating/monocrystal substrate interface. There may be defects which cause an interface potential and a Schottky barrier. Rectifying behavior is seen both in the samples with a large fraction of high pressure phase and in samples with a very low level high pressure phases, as indicated by X-ray diffraction. Photoconductivity is high in the vicinity of the coating edge (defined by a mask). The coating/substrate interface appears to provide efficient separation of charge carriers for photoconductivity. Theory and experiment will be discussed.

Acknowledgments:

This work was supported by the MRSEC program of the National Science Foundation under grant no. 9632570 through the Center for Thermal Spray Research.

4:45 PM V2.12

DEVELOPMENT OF NANOPARTICULATE MANGANESE DIOXIDE THIN FILMS AS NOVEL ELECTRODE MATERIALS OF ELECTROCHEMICAL CAPACITORS USING DIRECT WRITE TECHNOLOGIES. Suh-Cem Pang, Suk-Fun Chin and Marc A. Anderson, Water Chemistry Program, University of Wisconsin, Madison, WI.

The development of material precursors suitable for the fabrication of high power and energy density electrochemical capacitors using direct

write technologies is reported. Sol-gel-derived nanoparticulate manganese dioxide thin films in unbuffered electrolyte have been studied using electrochemical impedance spectroscopy (EIS) over the frequency range of 10 mHz to 100 kHz. These films showed a distinctive impedance response depending upon the range of frequencies: an almost purely capacitive behavior at low frequencies, a diffusion-controlled behavior at intermediate frequencies, and a purely resistive behavior at high frequencies. These frequency responses were independent of applied dc polarization potentials within the range of 0.0V to +0.9V versus SCE. Capacitance values of these films at various polarization conditions ranged from 2.6 mF/cm² to 4.5 mF/cm², with contributions from both the double-layer capacitance and pseudocapacitance associated with faradaic processes. While porous electrodes of nanoparticulate materials have resulted in an increase in their utilization, the distributive nature of such electrodes compromises their power delivery at high frequencies. The porous matrices of nanoparticulate MnO₂ systems allow only a fraction of the energy stored in such capacitor devices to be drawn at high frequencies. Though porous systems afford high surface areas and enhance the rate of kinetically slow reactions, they possess the inherent drawback of high resistivity associated with the pore electrolyte and the matrix. However, high capacitance values can possibly be achieved at high frequencies by significantly lowering the resistance of pore electrolyte, and by optimizing the microstructure such as the porosity, pore size distribution and film thickness. Our research focus has been directed toward optimizing the microstructure of sol-gel-derived nanoparticulate MnO₂ thin films, which possess frequency responses of fast charge and discharge required for pulsed power applications. The effects of suspension rheology, and the post-deposition laser-sintering conditions on the microstructure of MnO₂ thin films have been investigated.

SESSION V3/Y3: JOINT SESSION: DIRECT PATTERNING

Chairs: Duane Dimos and Douglas B. Chrisey
Tuesday Morning, April 25, 2000
Salon 12/13 (Marriott)

8:30 AM *V3.1/Y3.1

MATRIX ASSISTED PULSED LASER EVAPORATION DIRECT WRITE (MAPLE DW): A NEW METHOD TO RAPIDLY PROTOTYPE ACTIVE AND PASSIVE ELECTRONIC CIRCUIT ELEMENTS. D.B. Chrisey, A. Pique, J.M. Fitz-Gerald, R.C.Y. Auyeung, H.D. Wu, S. Lakeou and R. Chung, Naval Research Laboratory, Washington, DC.

We have developed a novel laser-based approach to do rapid prototyping of active and passive circuit elements called MAPLE DW. This technique is similar in its implementation to laser induced forward transfer (LIFT), but different in terms of the fundamental transfer mechanism and materials used. In MAPLE DW, a focussed pulsed laser beam interacts with a composite target on a laser transparent support or ribbon. Ideally, the laser energy causes the particulate and organic target material to be transferred to the substrate to form an adherent and conformal coating with minimal modification. Subsequent laser annealing, preferably in situ, is required to fully densify the coating and remove residual organic material. MAPLE DW is carried out at room temperature and atmospheric pressure and it has been demonstrated to work with many different classes of materials (e.g., metals, dielectrics, ferroelectrics, ferrites, polymers, and organics) and to <10-micron resolution. The final properties of the materials deposited depend on the deposition conditions and materials used, but when optimized, the properties are competitive with other comparable rapid prototyping techniques. Also, because the firing of the laser and the workpiece and substrate motion is computer automated, this technique is CAD/CAM compatible. A survey of the prototype devices fabricated by MAPLE DW, as well as a comprehensive description of the transfer mechanism, will be given.

9:00 AM V3.2/Y3.2

PATTERN WRITING BY IMPLANTATION IN A LARGE-SCALE PLASMA SOURCE IMMERSSED ION IMPLANTATION SYSTEM WITH A PLANAR RFI PLASMA SOURCE. Lingling Wu, Dennis M. Manos, College of William and Mary, Department of Applied Science, Williamsburg, VA.

A large-scale plasma source immersed ion implantation (PSII) system with planar coil RFI plasma source has been used to study an inkless, deposition-free, mask-based surface conversion patterning as an alternative to direct writing techniques on large-area substrates by implantation. The apparatus has a chamber 0.61m in diameter and 0.51m tall, with a base pressure in the 10^{-8} torr range, making it one of the largest available PSII systems. The system uses a 0.43m diameter planar rf antenna to produce dense plasmas capable of

large-area, uniform materials treatment. The process causes minimal dimensional change, avoids thermal distortion of the written surface profiles and can treat nonplanar surfaces simultaneously without tilting or rotating. Metallic and semiconductor samples have been implanted with various plasma compositions to produce small geometric patterns of interest for device manufacturing. Samples are characterized by variable-angle spectrometric ellipsometry (VASE), SEM, AES, SIMS, and XPS, and for electrical and mechanical properties. Experimental depth profiles are in good agreement with Monte-Carlo calculations (Profile Code), showing layer-like nitrogen depth profile with implanted nitrogen concentration around the stoichiometry level. Measured linewidth and profiles are compared to the mask features to assess lateral diffusion, pattern transfer fidelity, and wall-effects. The paper presents the results of MC-hybrid and PIC calculations of the flux and angles of ion trajectories through the boundary layer. The uniformity of flux as a function of (3-D) location on targets is one output of these calculations. The calculation also modeled the sheath expansion and helped to assess the fidelity of pattern transfer as a function of feature size. The model calculations are also able to predict the uniformity of implanted dose within small features such as trenches and vias.

9:15 AM *V3.3/Y3.3

LASER AND FOCUSED ION BEAM DIRECT-WRITE GROWTH OF 3-DIMENSIONAL MICRO- AND NANOSTRUCTURES.

M. Stuke, K. Kahlke, K. Mueller, A. Schertel Max-Planck-Institut f. biophys. Chemie, Goettingen, GERMANY.

Three different regimes of direct-write growth will be discussed: (1) growth of ceramics from gas phase precursor mixtures including dimethylethylamine/alane/oxygen and continuous wave/pulsed laser surface exposure in the visible resulting, with high growth rate, in complex three-dimensional aluminum oxide structures, which - if required - can be metallized with platinum using gas phase Pt(PF₃)₄, (2) metal growth from surface adsorbed precursors and pulsed UV laser exposure with short pulses, (3) growth of metals from surface adsorbed precursors including W(CO)₆ and focussed Ga ion beam exposure yielding tungsten structures with down to sub-100 nm precision. Examples and applications will be presented.

9:45 AM V3.4/Y3.4

INK-JET DEPOSITION OF CERAMIC SLURRIES. N. Reis, B. Derby, UMIST, Manchester Materials Science Centre, UNITED KINGDOM.

We have successfully printed green ceramic objects from slurries of Al₂O₃ dispersed in a paraffin wax using a commercial ink-jet printer developed for pattern making (Sanders Modelmaker 6-PRO). Ceramic suspensions are generally more viscous than the fluids normally passed through ink-jet heads. This may alter the response of the ink-jet printing system to its process parameters, e.g. driving voltage and frequency. We have explored the influence of fluid properties on ink-jet behaviour using CFD modelling and a parallel experimental study to determine the optimum ink-jet printing conditions for ceramic suspensions.

10:00 AM V3.5/Y3.5

LATERAL REDISTRIBUTION AND FILM PROFILES DURING INK-JET PRINTING OF POLYMER LED's. T.R. Hebner, B. Diamond, F. Pschenitzka, C. Madigan, X. Jiang, R. Register, S. Troian and J.C. Sturm, Center for Photonics and Optoelectronic Materials, Princeton University, Princeton, NJ.

The direct patterned deposition by ink-jet printing of polymers is an attractive option for forming patterned areas of thin polymer films with different light emitting properties (red, green, blue) for organic LED flat panel displays [1-2]. Conventional deposition techniques such as spin-coating lead to blanket films of a single color, and subsequent patterning of blanket films is difficult. For ink-jet printing of polymer LED's, one deposits a solvent droplet with the dissolved desired materials on an impermeable surface (e.g. indium tin oxide). The final profile of the deposited materials will critically depend on the redistribution of the dissolved molecules and polymers within the solvent droplet during the drying process. During drying, the liquid can flow within the droplet due to thermally-driven and convective-driven flows. In this paper, we examine the effect of such flows on the lateral distributions of organic dyes and small electron transport molecules in the final polymer film. When edge-pinning of the droplet occurs during drying, such flows can lead to a severe segregation of the dyes and molecules to the edge of the film, such that less than 1% of them remain in the active structure. This effect has been probed by photoluminescence and also by an X-ray microprobe. The effect can be overcome by reducing the driving force for the lateral segregation by reducing the deposition temperature of the droplets, or by chemically bonding the molecules to a polymer backbone. Both methods have been demonstrated successfully in LED's practice, which will be discussed.

1. T.R. Hebner and J.C. Sturm, Appl. Phys. Lett. vol. 73, 1775-1777 (1998).

2. S.-C. Chang, J. Bharathan, Y. Yang, R. Helgeson, F. Wudl, M.B. Ramey and J.R. Reynolds, Appl. Phys. Lett. vol. 73, 2561-2563 (1998).

10:30 AM V3.6/Y3.6

CALCULATION OF HAMAKER CONSTANTS IN NON-AQUEOUS FLUID MEDIA. Nelson S. Bell and Duane Dimos, Sandia National Laboratories, Albuquerque, NM.

Colloidal processing of materials is a necessary component of many new techniques for freeform solids fabrication. The design of a solid-liquid system for creating an optimal dispersion must balance the advantages and disadvantages of material solubility, solvent viscosity and solvent boiling point/vapor pressure. Information on the effect of solvent choice on the van der Waals interaction between materials is not readily available for many systems other than water. This talk will discuss the calculation of Hamaker constants from spectroscopic information available in the literature, present Hamaker constants for several nonaqueous systems, and give some experimental results regarding the choice of a fluid system on solid freeform deposition for sample materials in the electronics industry.

10:45 AM V3.7/Y3.7

NANOTECHTONIC PRINTING: DIRECT PATTERNING OF NANOPARTICLE INKS TO FORM FUNCTIONAL LOGIC AND MICRO-ELECTRO-MECHANICAL SYSTEMS. Colin Bulthaupt, Sawyer Fuller, Eric Wilhelm, Saul Griffith, Brent Ridley, Brian Hubert, Joseph Jacobson, MIT, Media Lab, Cambridge, MA.

Recently (Science, 286,746, October 22, 1999) we demonstrated an all-inorganic field effect transistor fabricated by printing. This was accomplished by developing a novel nanoparticle ink material and led to the highest mobility transistor which has yet been demonstrated by printing. The term nanotectonics refers to building functional structures (both logical and mechanical) from such nanoparticle inks. In this paper we report on recent progress towards directly patterning such nanoparticle inks to create both logic and machines (micro-electro-mechanical).

11:00 AM *V3.8/Y3.8

RAPID PROTOTYPING OF PATTERNED FUNCTIONAL NANOSTRUCTURES. C. Jeffrey Brinker, Hongyou Fan, Yunfeng Lu,

Dhaval Doshi, Nicola Huesing and Gabriel P. Lopez, the University of New Mexico, Sandia National Laboratories, Advanced Materials Lab, Albuquerque, NM.

Beginning with a dilute, homogeneous solution of ethanol, water, surfactant, and soluble silica, we recently demonstrated the rapid, continuous formation of ordered mesostructured films by dip-coating. Preferential evaporation of ethanol enriches the depositing film in surfactant, water and silica, inducing micellization and the formation of a variety of ordered silica/surfactant mesophases (hexagonal, cubic, lamellar). This presentation will first provide a brief overview of our evaporation-induced self-assembly (EISA) approach and its extension to the preparation of hybrid, organic-functionalized silica frameworks as well as metal-silica and (organic) polymer-silica nanocomposite films and particles. Then we will discuss new results where we utilize such homogeneous silica/surfactant solutions as inks in a variety of rapid prototyping processes like micropen lithography, ink-jet printing, and selective de-wetting. As previously demonstrated for dip-coating, evaporation accompanying these writing processes drives self-assembly into ordered mesophases. The resulting materials exhibit form and function on multiple length scales: on the molecular scale, functional organic moieties are positioned on pore surfaces, on the mesoscale, mono-sized pores are organized into 1-, 2-, or 3-dimensional networks, providing size-selective accessibility from the gas or liquid phase, and on the macroscale, 2-dimensional arrays and fluidic or photonic systems may be defined. Finally by introduction of photosensitive molecules into the inks, we can write arbitrary patterns of photosensitive mesophases. A subsequent lithographic patterning step then can be used to photo-define different functionalities within the parent pattern, providing an efficient route to hierarchically organized functional materials.

11:30 AM V3.9/Y3.9

RAPID FABRICATION OF PATTERNED FUNCTIONAL NANOSTRUCTURES VIA DIRECT WRITING AND PRINTING.

Hongyou Fan, Yunfeng Lu, Scott T. Reed, Tom Baer, Randy Schunk, Gabriel P. Lopez and C. Jeffrey Brinker, The University of New Mexico/NSF Center for Micro-Engineered Materials, The Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM.

The ability to engineer ordered arrays of objects on multiple length

scales has potential for applications such as microelectronics, sensors, wave guides, and photonic lattices with tunable band gaps. Since the invention of surfactant templated mesoporous sieves in 1992, great progress has been made in controlling different mesophases in the form of powders, particles, fibers, and films. To date, although there have been several reports of patterned mesostructures, materials prepared have been limited to metal oxides with no specific functionality. For many of the envisioned applications of hierarchical materials in micro-systems, sensors, waveguides, photonics, and electronics, it is necessary to define both form and function on several length scales. In addition, the patterning strategies utilized so far require hours or even days for completion. Such slow processes are inherently difficult to implement in commercial environments. We present a series of new methods of producing patterns within seconds. Combining sol-gel chemistry, Evaporation-Induced Self-Assembly (EISA), and rapid prototyping techniques like pen lithography, ink-jet printing, and dip-coating on micro-contact printed substrates, we form hierarchically organized silica structures that exhibit order and function on multiple scales: on the molecular scale, functional organic moieties are positioned on pore surfaces, on the mesoscale, mono-sized pores are organized into 1-, 2-, or 3-dimensional networks, providing size-selective accessibility from the gas or liquid phase, and on the macroscale, 2-dimensional arrays and fluidic or photonic systems may be defined. These rapid patterning techniques establish for the first time a link between computer-aided design and rapid processing of self-assembled nanostructures.

11:45 AM V3.10/Y3.10

ELECTROSTATIC PRINTING, A VERSATILE MANUFACTURING PROCESS FOR THE ELECTRONICS INDUSTRIES. Robert H. Detig, Electrox Corporation, Denville, NJ.

Functional materials configured as liquid toners are printed on a variety of substrates for various manufacturing processes. The materials include metal toners, resistor toners, high k dielectric toners, phosphors and ITO. The substrates printed upon include glass, bare and coated metal, polymeric film and even paper. A fixed configuration electrostatic printing plate is used in most manufacturing applications though traditional photo receptor plates can be used if electronic addressability is desired. Applications of electrostatic printing for electronic packaging products (printed wiring boards and flex circuits) and of passive electronic components themselves will be shown. Possible applications of toners to the manufacture of flat panel displays will be discussed. Results with a pure silver toner printed on both glass and paper will be reported. Examples of passive electronic components like resistors, capacitors, and even inductors that have been electrostatically printed with liquid toners will be shown.

SESSION V4: PATTERNING AND METAL DEPOSITION

Chair: Henry Helvajian
Tuesday Afternoon, April 25, 2000
Salon 12 (Marriott)

1:30 PM *V4.1

DIRECT PATTERNING OF HYDROGENATED AMORPHOUS SILICON BY NEAR FIELD SCANNING OPTICAL MICROSCOPY. Russell E. Hollingsworth, Materials Research Group, Inc. Wheat Ridge, CO; Mary K. Herndon, William C. Bradford, Joseph D. Beach and Reuben T. Collins, Colorado School of Mines, Golden, CO.

Practical methods for directly patterning hydrogenated amorphous silicon (a-Si:H) films have been developed. Direct patterning involves selectively oxidizing the hydrogen passivated a-Si:H surface, with the oxide then serving as an etch mask for subsequent hydrogen plasma removal of the unoxidized regions. Photo induced oxidation has been extensively studied using both far field projected patterns and near field scanning optical microscopy (NSOM) for direct write patterning. Examination of the threshold dose for pattern generation for excitation wavelengths from 248 to 633nm provides indirect evidence for involvement of electron-hole recombination in optically induced oxidation. Optical exposure of a-Si:H in vacuum demonstrated that oxygen must be present in the ambient atmosphere during exposure for successful pattern generation. This suggests that oxidation of the surface may not involve removal of hydrogen, but rather breaking of Si-Si backbonds and insertion of oxygen. An additional mechanism for oxide generation was observed whereby pattern generation resulted from simple proximity of an NSOM probe within ~30nm from the sample surface. The probe dither amplitude was found to greatly affect the line width and height of patterns generated without light. Line widths of approximately 100nm, comparable to the probe diameter, were obtained.

2:00 PM V4.2

NANOSTRUCTURAL LITHOGRAPHY: WRITING OF

STRUCTURES AND FUNCTIONALITY IN PHOTOACTIVE THIN FILM SILICA MESOPHASES. Dhaval A. Doshi¹, Nicola Huesing², Renita Cook¹, Hongyou Fan¹, Alan J. Hurd³, C. Jeffrey Brinker^{1,3}. ¹University of New Mexico, Albuquerque, NM, ²Vienna University of Technology, Vienna, AUSTRIA, ³Sandia National Laboratories, Albuquerque, NM.

Control of structure on multiple length scales is evident in Nature and crucial to advances in micro- and nanotechnologies. Cooperative self-assembly processes of inorganic species and amphiphilic molecules afford an efficient means to build nanostructures and nanocomposites. Thin films are one of the most promising applications of so-called mesostructured materials, and the ability to build hierarchical structures and functionality is the key to their successful implementation in future micro-systems. Recently, so-called micro-contact printing (μ CP) and micro-molding in capillaries (MMIC) techniques have been used to create patterned thin film silica mesophases. Here we report a novel lithographic procedure that enables selective etching of silica mesophases (thereby serving as a 1-step negative resist process) and allows patterning of thin film mesostructure, refractive index, and wetting behavior. The process involves incorporation of a photoacid generator in the coating sol. Dip/spin coating results in the formation of a photoactive mesostructured thin film. Selective UV exposure, which can be achieved using a mask or via direct Laser writing, results in localized photoacid generation. We exploit the pH sensitivity of supra-molecular self-assembly by affecting the silica condensation kinetics and also the mesophase formation, to optically write structure and functionality in the film. Both ionic and non-ionic surfactant systems have explored and the work has been extended to the patterning of nanocomposites of hard (silica) and soft (polymer) components. The films are characterized using X-Ray diffraction, transmission and scanning electron microscopy, optical microscopy, ellipsometry, MAS-NMR and atomic force microscopy. Our ability to spatially control structure and function on several length scales is of interest for sensor arrays, nano-reactors, photonic and fluidic devices, and low dielectric constant films.

2:15 PM V4.3

COMPUTATIONAL MODELING OF DIRECT PRINT MICRO-LITHOGRAPHY. Anton A. Darhuber, Scott M. Miller, Sandra M. Troian, Princeton University, Dept. of Chemical Engineering; Sigurd Wagner, Princeton University, Dept. of Electrical Engineering, Princeton, NJ.

Using a combination of experiment and simulations, we have studied the equilibrium shapes of liquid microstructures on flat but chemically heterogeneous substrates. The surface patterns, which define regions of different surface energy, induce deformations of the liquid-solid contact line, which in turn can either promote or impede capillary break-up and bulge formation. We study numerically the influence of the adhesion energies on the hydrophilic and hydrophobic surface areas, the pattern geometry and the deposited fluid volume on the liquid surface profiles, as well as the effect of chemical or topological defects. Comparison of the computed shapes with glycerol microdroplets on a patterned silicon wafer has yielded excellent results. Experimentally, the chemical modulation corresponding to the surface patterns is defined with a self-assembled monolayer of octadecyltrichlorosilane on SiO₂ or hexadecanethiol on gold. As will be discussed, the simulations provide several important design rules. For instance, the pattern to be printed must not consist of vastly different length scales. In addition, the presence of surfactants can greatly improve edge resolution. Our results suggest a new, cost-effective and highly parallel approach for microlithography of significance to the fabrication of semiconductor devices, optical diffraction elements or fluid microreactors.

2:30 PM V4.4

HIGH-RESOLUTION ELECTRON BEAM PATTERNING USING TITANIUM ISOPROPOXIDE FILMS. William Mitchell, University of California, Dept of Electrical and Computer Engineering, Santa Barbara, CA; Evelyn Hu, University of California, QUEST and Dept of Electrical and Computer Engineering, Santa Barbara, CA.

The ability to deposit and pattern masks on a semiconductor substrate, transfer this pattern into the substrate via a low-damage etch, and then regrow a cladding/passivation layer, all within an ultrahigh vacuum (UHV) environment, would provide enormous flexibility in the production of a wide variety of 'air-sensitive' structures, e.g., structures that utilize quantum wire and dot arrays. We have previously shown that a thick, multilayer film of titanium isopropoxide condensed on a cold substrate exhibits excellent in-situ resist properties.¹ It is UHV compatible, low electron doses (order of 100's of μ C/cm²) convert the volatile precursor to a nonvolatile oxide deposit, and the deposited oxide is resistant to etching in Cl₂ at elevated substrate temperatures (350 °C). In this work, we utilize Auger electron spectroscopy and scanning electron microscopy to

investigate the spatial resolution capability of these condensed titanium isopropoxide layers on a cold ($< -20^{\circ}\text{C}$) GaAs substrate. We have found that both resolution and sensitivity strongly depend on the initial multilayer film thickness. The optimum condition determined with our experimental configuration resulted in a dot size of approximately $0.1\ \mu\text{m}$ by exposing a film 8-10 nm in thickness to an electron dose in the range of 0.1 pC/pixel. Films that were too thin (order of 1 nm thick) were inefficient resist and required a large electron beam dose ($> 10\ \text{pC/pixel}$) to effect observable deposition. Moreover, the produced dots were rough and poorly defined (with sizes on the order of $1\ \mu\text{m}$). Although exhibiting superior electron sensitivity (e.g., doses less than 0.1 pC/pixel were sufficient for deposition), films that were significantly greater than 10 nm in thickness exhibited poorer resolution for the electron exposures investigated, i.e., dot sizes $\geq 1\ \mu\text{m}$. Possible origins of the observed behavior, in terms of electron backscattering and secondary electron emission, will be discussed.

¹W. Mitchell and E. Hu, J. Vac. Sci. Technol. B17, 1622 (1999).

2:45 PM V4.5

MICROPEN DIRECT WRITE FABRICATION OF MULTILAYER CAPACITORS AND INTEGRATED PASSIVES. P.G. Clem, B.A. Tuttle, P. Yang, N.S. Bell and D.B. Dimos, Sandia National Laboratories, Albuquerque, NM; G.L. Brenneka, University of Missouri, Rolla, MO; S.L. Morissette, MIT, Cambridge, MA.

Emphasis on small size for portable electronics places priority on novel materials, component miniaturization, and increased levels of circuit integration. In our research, we have developed several approaches toward integration of multilayer LTCC and sub-200C processed passive components, including high value capacitors and inductors, and high precision resistors. In one approach, direct writing of ceramic powder slurries by a commercial CAD/CAM MicroPen instrument has enabled integration of single and multilayer capacitors of high dielectric constant ($K' > 1000$) X7R BaTiO₃ thick films and electrodes. Specifics of slurry development and microstructural and stress evolution will be discussed. Approaches to low temperature preparation of low frequency and RF dielectrics and use of Micropen direct writing for rapid prototyping will also be presented. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94A185000.

3:15 PM *V4.6

REAL-WORLD APPLICATIONS OF LASER MICROCHEMICAL DIRECT WRITING. Daniel J. Ehrlich, Revise Inc., Burlington, MA.

This paper will review recently successful real-world applications of laser microchemical direct writing methods. We will draw on areas of integrated circuit prototyping, failure analysis, and *in situ* trimming. We will illustrate with specific examples from the contrasting areas of microprocessors and microelectromechanical systems (MEMS). Recent trends in microelectronics, including the dramatic recent shift to flip-chip electronic packages, have been accelerated in a small but significant part by solutions provided by the laser direct writing technology. Similarly, laser microchemical direct writing provides best solutions for several fairly general problems in the development of MEMS products. We will review the microreactions used and identify areas where improved reaction chemistry or new mechanisms would be useful. A further recent trend is intense competition in portable electronics, such as cell phones, global positioning systems and smart cards. This has created opportunities for new laser reactions designed for applications in system modification on polymer and ceramic packages, in close analogy to the semiconductor applications above but requiring different reaction chemistry.

3:45 PM V4.7

CONVECTIVE FLOW SPLITTING OF PRINTED COPPER LINES. Tanja Cuk, C.M. Hong, Sandra Troian, Sigurd Wagner, Princeton University, Dept of Electrical Engineering and Dept of Chemical Engineering, Princeton, NJ.

We have developed a technique for the jet printing of copper lines using solutions of a metal organic precursor, copper hexanoate. An $80\text{-}\mu\text{m}$ wide jet printed liquid line is observed to split into two $20\text{-}\mu\text{m}$ wide lines, which can be converted to copper lines of $\sim 10\ \mu\Omega\text{-cm}$ resistivity by a 200°C process. We observe further splitting into four parallel lines in experiments with written lines of copper hexanoate solution in chloroform. The positions and profiles of the double or quadruple lines of copper hexanoate are symmetric about the axis of the initial liquid line. This spontaneous splitting could provide a path toward the printing of high resolution copper patterns by low resolution jetting. Either surface energy or buoyancy may drive the convection that produces the line splitting. We measured surface tension, density, evaporation rate, contact angle and viscosity as functions of the solute concentration. The data make evident that the Marangoni number (for surface energy) is orders of magnitude larger

than the Rayleigh number (for buoyancy). Therefore the lines split by surface energy driven convection, with the Marangoni number changing by an order of magnitude over our experimental conditions. The cause of this change in the Marangoni number is the variation of the viscosity of our solutions by a factor of six. Between the splitting into two and four lines we observe a clear phase transition. The viscosity controls the multiplicity of splits and this phase transition. High concentration / high viscosity 'ink' splits into two lines, whereas low concentration / low viscosity produces four lines. We are now studying the line splitting process in real time, and will report results at the Symposium.

4:00 PM V4.8

HIGH RESOLUTION COPPER LINES BY DIRECT IMPRINTING. C.M. Hong, X. Sun, S.Y. Chou, S. Wagner, Princeton University, Department of Electrical Engineering, Princeton, NJ.

We report the first high resolution imprinting of metal. A soft metal organic precursor layer is imprinted first. Then the imprinted pattern is converted to metal. The process demonstrates that metal patterns can be made by imprinting directly, without the need for photolithography, etching, or lift-off. We begin by spinning a layer of copper hexanoate onto a glass substrate. This layer is imprinted with a mold to form lines with width and spacing down to $1\text{-}\mu\text{m}$. The molding is made possible by the soap-like flow of the copper hexanoate. These lines then are converted to metallic copper in two steps. In the first step the copper hexanoate is decomposed by heating at 200°C to a mixture of copper and copper oxide. In the second step the lines are converted to pure copper by annealing at 200°C in a mixture of hydrogen and nitrogen. Optical micrographs and atomic force micrographs/profiles show clearly resolved lines of the precursor copper hexanoate. The lines of converted copper metal are narrower and thinner than those of the precursor. Their grain size, determined from X-ray line width, is $\sim 40\ \text{nm}$. The resistivity of the copper lines is $8\ \mu\Omega\text{-cm}$. Thus the imprinting of a copper organic precursor provides a route for the direct patterning of high-resolution low-resistivity copper conductors.

4:15 PM V4.9

NANOPARTICLE BASED DIRECT WRITE METALLIZATIONS FOR PHOTOVOLTAIC DEVICES. David Ginley, Calvin Curtis, Doug Shulz, Tanya Rivkin, National Renewable Energy Laboratory; Fred Tepper Argonide Corporation; Jason Underwood, Florida Institute of Technology.

The development of direct write low cost approaches to large area and medium resolution ($> 10\ \mu$) contacts lends itself well to the application of nanoparticle based inks. We will discuss our recent results on the application of such inks for metallizations in photovoltaics and microelectronics. Metal powders were generated by the electroexplosion of wire process both in Russia and in the US. Inks were prepared from Ag, Cu and Al. In some cases surface oxide was removed chemically and the surface stabilized through the application of chelating ligands. Direct Write approaches were investigated for large area metallizations and patterned metallizations. For large area deposition inks were deposited by spray deposition and for fine line applications ink-jet direct writing was investigated. In some cases where adhesion proved difficult an alternative approach was employed. In the case of Cu and Ni we also explored the ink-jet deposition of catalytic metal lines (Pt) followed by electroless metal deposition. Lines with resolution less $100\ \mu\text{m}$ could be obtained by this approach. In all cases after anneal good ohmic contacts could be obtained.

4:30 PM V4.10

DIRECT WRITE TECHNIQUES FOR FABRICATING UNIQUE ANTENNAS. Robert Taylor, Kenneth Church, CMS Technetronics Inc, Stillwater, OK; James Culver, Raytheon Corporation, St. Petersburg, FL.

The fabrication of many antennas is limited to the precision and skill given by individual laborers. This is slow and many times creates inconsistent results. As the desire for higher frequencies in RF transmitters and receivers increase the physical dimensions of the supporting antennas decrease. This adds new complexities to the fabrication of these antennas. Several designs, which may be considered high performing antennas, are difficult to reproduce and many times cannot be fabricated at all due to the sophisticated patterning and precision necessary for success. A combination of Laser Chemical Vapor Deposition (LCVD) and Laser Sintering (LS) of pastes provides the necessary tools to fabricate unique patterns in two and three dimensions. A brief summary of various antennas will be given with the necessary steps to fabricate these using the advanced direct write techniques. A demonstration of a direct write fabricated antenna will also be presented for review.

4:45 PM V4.11

FOCUSED ELECTRON BEAM INDUCED DEPOSITION OF GOLD

AND RHODIUM. P. Hoffmann¹, I. Utke², B. Dwir², K. Leifer², F. Cicoira¹, P. Doppelt³, E. Kapon². ¹Microengineering and ²Physics Departments, Swiss Federal Institute of Technology Lausanne, EPFL, ³Ecole Supérieure de Physique et Chimie Industrielle, C.N.R.S., Paris, FRANCE.

Electron-beam induced deposition (EBID) offers unique advantages over classical resist-based processes. Amongst these are the possibility of in-situ deposition of metals and insulators, as well as selective etching, during one cycle; the deposition of high aspect ratio columnar structures [1], air-bridges and other 3D features; and the insensitivity to surface features (large depth of field). In this work, we compare two EBID precursors of the same halogen trifluorophosphine family with two different metals, Rhodium and Gold, concerning their decomposition with focused electrons. Our system is based on a Cambridge S100 SEM with tungsten filament, operating at 25kV. Typical beam diameter is 20 nm at 4pA probe current, 800 nm at 8nA maximum current. The SEM is controlled by a Nabity Systems NPGS software running on a PC. The specimen chamber background pressure is $2 \cdot 10^{-6}$ mbar. For EBID, we introduced a metal precursor to the surface of the sample by either a micro-tube pointing to the substrate and connected to an external precursor supply, or an internal syringe reservoir containing the precursor. The working pressure in presence of a precursor was up to $3 \cdot 10^{-4}$ mbar. The substrate holder and internal reservoir could be independently heated or cooled in the range of 0 - 150°C. As substrates we used mostly SiO₂ - coated Si wafers, with Au electrodes for resistivity measurement. Metal containing lines were deposited using the carbon-free [RhCl(PF₃)₂]₂ as precursor for EBID. The measured vapor pressure of the precursor at room temperature is $7.4 \cdot 10^{-2}$ mbar[2]. TEM images allow the determination of the Rh cluster size that depends on the electron beam current used to induce the deposition. Auger electron analysis shows that the deposited lines contain about 40% Rh. With PF₃AuCl as precursor, deposition resulted in highly electrically conducting lines with electrical resistivities as low as 22 $\Omega/\mu\text{m}$. Percolation of the gold clusters during deposition is shown by ex-situ TEM studies. [1] C. Schoessler, J. Urban and H. W. P. Koops, "Conductive Supertips for Scanning Probe Applications", *J. Vac. Sci. Technol. B*, 15, 1535-1538 (1997) [2] F. Cicoira, T. Ohta, P. Doppelt, L. Beitone and P. Hoffmann, "Static vapor pressure measurement of organometallic precursors for molecular vapor deposition processes", *to be published*, (1999).

SESSION V5/J4: JOINT SESSION:
LASER DIRECT WRITING
Chair: Herbert Herman
Wednesday Morning, April 26, 2000
Nob Hill C/D (Marriott)

NOTE EARLY START

8:15 AM V5.1/J4.1

AN IMPROVED METHOD OF UV LASER DIRECT-WRITE DEPOSITION OF MATERIALS FOR MICROELECTRONICS APPLICATIONS. K.M.A. Rahman, D.N. Wells and M.T. Duignan, Potomac Photonics, Inc., Lanham, MD.

We demonstrate a maskless laser direct-write method, a process that transfers materials directly from a ribbon to a substrate, thereby enabling feature widths as small as few microns. This process offers the promise of fabricating interconnects and passive electronic components at a high speed, however, there are practical challenges that must be addressed for promoting the process from research scale to production. The main steps in this direct-write method are the following. First, an ink is formulated with the material to be transferred as the main ingredient; the ink is then applied to a ribbon. The ribbon is then used under ambient conditions to deposit elements on a substrate. This is done by irradiating the ribbon with a laser beam of known fluence, spot size and duration suitable for the particular ink. The main challenges in this process are successful transfer of the ink from the ribbon and its effective adhesion to the substrate. A post-deposition annealing is also necessary in order to achieve proper densification, as the electrical properties of transferred features are function of their morphological details. We have worked out a method that integrates the deposition and annealing processes on a single machine. This direct write method uses a micromachining system with adjustments for ribbon and substrate manipulations. Conducting lines deposited from Ag ink on several substrate materials by this method under ambient conditions were found to produce good adhesion and desirable electrical properties. Further investigations are underway in order to study the main controlling factors such as surface chemistry, partial melting of the substrate during deposition, proper annealing conditions and other factors pertaining UV laser parameters.

8:30 AM *V5.2/J4.2

LASER GUIDED DIRECT WRITING OF ELECTRONIC COMPONENTS. Michael J. Renn, Marcelino Essien, Bruce H. King and W. Doyle Miller, Optomec Design Company, Albuquerque, NM.

The extreme brightness and submicron localization possible with lasers make them powerful tools for modifying materials on the micron scale. While traditional electronic material processing involves high temperature treatments at times ranging from minutes to hours, laser direct writing occurs at low temperature (~ 200 C) and short time scales (< 10 ms). As a result, new colloidal and liquid precursors must be developed to meet these conditions. Optomec is developing a new, laser-based technique for dispensing and processing liquid and colloidal materials on virtually any substrate. This paper will summarize recent results including precursor development and laser processing of various metals and dielectrics. Metal line deposits of Pt, Au, Cu, Ag, and Rh have been written with 10 micron \pm 1 micron feature size and resistance values of $< 10 \times$ bulk. Likewise, single phase, barium titanate has been densified at low processing temperature. Deposition has been demonstrated on a wide range of substrates including alumina, glass, polyimide, barium titanate, PVC plastic, and various metals.

9:00 AM V5.3/J4.3

LASER INDUCED ETCHING OF Si WITH NF₃ USING CuBr LASER. B. Ivanov¹, M.P. Tarassov², L. Zambov¹. ¹Dept. of Semiconductors, University of Chemical Technology and Metallurgy, Sofia, BULGARIA, ²Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Science, Sofia, BULGARIA.

Laser induced etching of Si with NF₃ were investigated using the focused beam of copper bromide vapor laser with wavelengths of 510 and 578 nm in vacuum system. The laser average power was in the range 4-10 W with repetition rate - 20 kHz and the pulse duration - 60 ns. NF₃ was used at partial pressure in the range 1 - 1000 mbar. The basic process parameters were varied in the ranges: scanning speed from 5 to 400 ($\mu\text{m/s}$) and substrate temperature of 100 and 400°C, respectively. The etched structures were investigated by Scanning Electron Microscopy (SEM). The influence of the process parameters - laser power, scanning speed, NF₃ pressure and background temperature of the width and depth of etched grooves was studied. The etched rates was in the range 0.5 - 25 $\mu\text{m/s}$.

9:15 AM *V5.4/J4.4

PHOTO-INDUCED LARGE AREA GROWTH OF DIELECTRICS WITH EXCIMER LAMPS. Ian W. Boyd, Electronic & Electrical Engineering, University College, London, London, UNITED KINGDOM.

In this paper, the principles and properties of novel vacuum ultraviolet (VUV) and ultraviolet (UV) radiation generated by novel excimer sources are discussed. Compared with conventional sources, these excimer lamps offer narrow-band radiation at various wavelengths from 108 - 354nm and over large areas. Since excimer complexes have no stable ground states self-absorption of the emitted radiation in the discharge is avoided. As a consequence, high efficiencies at high power densities can be achieved. The variety of available wavelengths offers an enormous potential for new industrial applications in materials processing. Previously, photo-oxidation of silicon, germanium and silicon germanium and photo-deposition of single- and multi-layered films of silicon oxide, silicon nitride, and silicon oxynitride have been demonstrated. In this paper, UV-induced growth of high dielectric constant (tantalum oxide, titania, or PZT) and low dielectric constant (polyimide and porous silica) thin films by photo-CVD and sol-gel processing, as well as the effect of low temperature UV annealing, are discussed. Film properties, determined using ellipsometry, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV spectrophotometry, scanning electron microscopy (SEM), and electrical characterisation, showed that good quality layers could be produced. Leakage current densities as low as 0.9 pA/sq.cm and 32 $\mu\text{A/sq.cm}$ have been obtained for the as-grown tantalum oxide films formed by photo-induced processing and photo-CVD, respectively - several orders of magnitude lower than for other as-grown films prepared by any other technique. A subsequent low temperature (400°C) UV annealing step improves these to 2nA/sq.cm at 0.5 MV/cm and 7nA/sqcm, respectively. These values are essentially identical to those only previously obtained for films deposited by alternative methods and annealed at temperatures between 600 and 1000°C. The applications investigated so far clearly demonstrate that low cost high power excimer lamp systems can provide an interesting alternative to conventional UV lamps and excimer lasers for industrial large-scale low temperature materials processing.

9:45 AM V5.5/J4.5

LASER DIRECT WRITE OF CONDUCTING AND INSULATING TRACKS IN SILICON CARBIDE. Deepak Sengupta and Aravinda Kar, Laser-Aided Manufacturing, Materials and Micro-Processing Laboratory, School of Optics and Center for Research and Education in Optics & Lasers (CREOL), The University of Central Florida, Orlando, FL; Nathaniel R. Quick, Applicote Associates, Lake Mary, FL.

Lasers were used to directly generate conducting tracks in silicon carbide bulk and thin film conformal surfaces. Conductor resistivities as low as $10E-4$ ohm-cm are produced from insulating substrate with an initial resistivity of $10E11$ ohm-cm. However, in the presence of pure oxygen, laser-irradiated silicon carbide semiconductor and conductor phases exhibit insulating characteristics. Analytical procedures such as SEM, JOEL Super Probe 733, Raman Spectroscopy, AFM, and Auger were examined for the evaluation of the mechanism for the electrical property conversion in these laser processed materials. This technique of laser writing conducting, semiconducting and insulating paths on silicon carbide leads to basic electronic material combinations necessary to fabricate sensors and electronic devices. The criteria for extending this technology to other ceramic bulk and thin film conformal surfaces will be discussed.

10:15 AM V5.6/J4.6

LASER GUIDED DIRECT WRITING. Robert Pastel, Peter Geiser, Edward Nadgorny, Dept of Physics; Allan Struthers, Math. Sci. Dept, Michigan Technological University, Houghton, MI.

A new technique for direct write technologies, Laser Guided Direct Write (LGDW), uses lasers to guide and deposit particles on to a variety of substrates. The technique is quite general; we have guided and deposited dielectric and metal particles, and droplets onto glass, sapphire, plastic, and ceramic substrates. The particle sizes range from several hundred nanometers to several microns. LGDW constructs structures by repetitive deposition of particles while translating the substrate, and can construct electrical components with layered structures. The process can operate at atmospheric pressure and room temperature, and can be adjusted to control the particle and substrate temperature. The scattering and absorption of the laser light by the particles produces optical forces that confine the particle transversely within the laser beam and propel the particle along the laser propagation axis. The accuracy and definition of the deposited structure is crucial for commercial development of this technique. The accuracy is determined by numerous factors including: the transverse optical force which is proportional to laser power; radiometric forces arising from laser heating of particle and substrate, Brownian forces, and generated convective flows. We measure the deposition accuracy of LGDW by in-situ microscopic monitoring of the process. The deposition accuracy is measured for different particle and substrate materials, transport distance, and laser power. Deposition accuracy is inversely proportional to transport distance and directly proportional to the refractive index for dielectric particles. A vertical bias in the deposition patterns indicates thermal convection effects. Experimentally the deposition accuracy is independent of laser power. Possible mechanisms for this unusual result will be discussed.

10:30 AM V5.7/J4.7

CFD MODELING OF LASER GUIDED PARTICLE DEPOSITION FOR DIRECT-WRITE FABRICATION. J.C. Sheu and M.G. Giridharan, CFD Research Corp., Huntsville, AL.

Direct-write processes for producing multi-layer RF modules depend on a number of complex interacting physical phenomena with varying time scales. Physical phenomena such as particle transport, power absorption from laser, particle melting and solidification, substrate heating, surrounding air motion, etc need to be controlled precisely in order to optimize the deposition process. Experiments to solve these issues are prohibitively expensive and time consuming. A CFD modeling tool will be an efficient tool in providing insight into the complex interactions between these processes as well as identifying optimum conditions and processes for laser-based fabrication. This paper reports the progress made in developing a CFD based modeling tool. An Eulerian-Lagrangian two-phase approach is used to predict the behavior of particles from the delivery system to the substrate through the optical hollow fiber guidance system. The particle capturing performance, particle heat transfer and phase change, laser heating of substrate have been studied. The results indicate that buoyancy induced air flow due to laser heating of opaque substrates deflects the particles away from the substrate. This limits the writing speed and substrate materials. But various techniques for overcoming this problem including proper orientation of the system and low pressure operation have been identified and demonstrated with simulation results.

10:45 AM *V5.8/J4.8

NOVEL METHOD FOR LASER DIRECT WRITING MESOSCOPIC CONFORMAL ELECTRONIC DEVICES AND SENSORS.

James M. Fitz-Gerald, A. Piqué, R.C.Y. Auyeung, H.D. Wu, S. Lakeou, D.B. Chrisey, Naval Research Laboratory, Washington, DC.

Attention to the field of non-lithographic processing has increased in recent years in response to a need to develop a rapid prototyping technique that is capable of rapidly fabricating integrated electronic devices and sensors, ranging in size from 5 -200 microns. We present a novel method to direct write materials onto planar and non-planar substrates at room temperature and under atmospheric pressure. The process utilizes using a pulsed laser to transfer material from a donor ribbon onto an acceptor substrate with a feature resolution of 5 microns. The donor ribbon consists of a 2 quartz wafer with a single side coated with a powder and/or a metal organic precursor of interest (metals, ferrites, ferroelectrics, etc.). The transfer efficiency and resolution have been determined as a function of the ribbon manufacture properties, laser fluence, material properties, and the transfer distance between the donor ribbon and the acceptor substrate. Donor ribbons were manufactured with metal organic precursors alone and in combination with powders to further enhance substrate adhesion and bulk density properties. A pulsed excimer laser ($\lambda = 248$ nm) was focused down to average spot sizes ranging from 10 - 100 microns with fluences ranging from 0.5 to 2 J/cm² at repetition rates between 1-20 Hz. Glass, alumina, duriod and silicon ranging in thickness from 75 microns - 1 mm were used as substrates. Metallic and complex oxide materials were transferred in single and multi-layer fashion to form capacitors, resistors, conductors, and inductors on the mesoscopic scale successfully. In-situ and ex-situ annealing of the transferred materials was performed by both pulsed ND: YAG laser ($\lambda = 1.06$ microns) and conventional furnace heat treatments at 250°C to increase the substrate adhesion and to transform the metal organic while removing the organic precursor material. Chemical composition analysis was performed by X-ray diffraction. Morphological characterization was performed by scanning electron microscopy and 3-D surface profilometry. Electrical characterization was performed with a HP 4291B Impedance Analyzer.

11:15 AM V5.9/J4.9

LASER PROCESSING OF PARMOD FUNCTIONAL ELECTRONIC MATERIALS. Paul H. Kydd, David L. Richard, Parelec, Inc. Rocky Hill, NJ; Kenneth H. Church, CMS Technetronics, Stillwater, OK; Douglas B. Chrisey, Naval Research Laboratory, Washington, DC.

Parmod is a family of materials which can be printed and thermally cured to create metallic conductors on printed wiring boards. This additive process provides a way to produce circuitry direct from CAD files without intermediate tooling of any kind. The printed image is converted to pure metallic traces in seconds at a temperature low enough to be compatible with commonly used rigid and flexible polymer-based substrates. This simple two-step process eliminates the hazardous wastes and employee health & safety issues associated with conventional plate-and-etch photolithographic technology. Recently the Parmod technology has been extended from metals to oxides to enable printing passive electronic components such as resistors, capacitors and inductors as well as the metallic interconnects between them. While thermal curing of the oxides provides useable electronic properties, particularly of resistors and capacitors, the performance of all these novel materials could be improved by laser processing. This paper discusses preliminary results on laser processing of Parmod conductors and components in two different systems.

11:30 AM V5.10/J4.10

NUMERICAL SIMULATION OF LASER INDUCED SUBSTRATE HEATING FOR DIRECT WRITE OF MESOSCOPIC INTEGRATED CONFORMAL ELECTRONICS (MICE). Sam Lowry, Sandip Mazumder, J.C. Sheu, CFDR, Huntsville, AL; Robert Stewart, CMS Technetronics Inc., Stillwater, OK.

Laser processing of selected precursors enables the direct deposition of electronic components onto diverse substrate materials. This technique is being developed by CMS Technetronics to allow the direct write of Mesoscopic Integrated Conformal Electronics (MICE). For complex circuits, controlling the temperature during the deposition process is critical and potentially difficult when a range of thermal and optical material properties is involved. In support of the laser write process, a numerical model is used to simulate the optical and thermal interaction of selected lasers with the precursor/substrate. The model couples Monte Carlo and Discrete Ordinate Method (DOM) radiation models with a multi-physics CFD code to predict the conductive, convective, and radiative heat transport in the system. In addition to including the effects of thermal properties, the model also accounts for the optical effects of reflection and absorption as functions of both temperature and wavelength. A brief overview of the numerical model is provided. Selected simulations are presented along with empirical

validation. The capabilities, limitations, and potential applications of the model with respect to MICE are discussed.

11:45 AM V5.11/J4.11

THERMAL STABILITY AND ANALYSIS OF LASER DEPOSITED PLATINUM FILMS. G.J. Berry, J.A. Cairns, M.R. Davidson, Y.C. Fan, A.G. Fitzgerald, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee, UNITED KINGDOM; A.H. Fzea, J. Lobban, P. McGivern, J. Thomson, Department of Chemistry, University of Dundee, Dundee, UNITED KINGDOM; W. Shaikh, Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UNITED KINGDOM.

As the trend towards device miniaturisation continues, surface effects and the thermal stability of metal deposits become increasingly important. We present here a study of the morphology and composition of platinum films, produced by the UV induced decomposition of organometallic materials, under various annealing conditions. The surface composition of the metal deposits was studied by X-ray photoelectron spectroscopy, both as-deposited and following thermal treatment. In addition, the morphology of the surface was studied by atomic force microscopy which enabled the investigation of film restructuring. These studies were performed over a range of temperatures up to 1000°C and in oxidising and reducing atmospheres. Complementary information regarding the changes in film morphology has been obtained from transmission electron microscopy. This data has been used to provide an insight into the effects of elevated temperatures on metal films deposited by a direct write method.