SYMPOSIUM V
Materials Development for Direct Write Technologies
April 24 – 26, 2000

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SESSION VI: OVERVIEW OF DIRECT WRITE
Chair: Douglas B. Chrisey
Mass Morning, April 3, 2000
Salon 12 (Marriott)

8:30 AM #VI.1
THE POTENTIAL OF DIRECT-WRITE TECHNOLOGIES.
William L. Warren, DARPA, Arlington, VA.

The goal of the DARPA MICT (mesoscopic integrated conformal electronics) program is to develop small, low-cost processes for 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 transistors, and interconnects, etc.) Multiple parallel and sequential processes develop a system capable of high frequency circuitry. The MICT direct-write machine is a key tool used to fabricate circuits and passive components based on thin-film titanium nitride with sputtered dielectric layers of 50 nm with resistivities of 78 ohm.cm, and resistors having sheet resistances in the range of 50 Ohm/sq to 1KOhm/sq. Hybrid thermal spraying systems have allowed us to fabricate high temperature circuitry. 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 in 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 compounds 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; Thickness 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 #VI.4
CHARGED METAL MOLTEN-DROP DEPOSITION AS DIRECT WRITE TECHNOLOGY. Melissa Otman, Qingbin Liu, Zhan Zhu, Robert Smith, University of California, Irvine, Department of Mechanical and Aerospace Engineering, Irvine, CA.

The formation and control of highly uniform charged metal droplets from a capillary stream breakup 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 breakup, and the unparalleled uniformity of droplets 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 electronically charged and deflected onto a substrate with a measured accuracy of ±12.5µm. 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 material properties of the printed artifact.

The factors that affect the geometric fidelity of the deposit include: attainment of desired electrostatic charge, mutual electrostatic interactions between charged droplets, and aerodynamic effects allowing droplet flight to a substrate. In addition, the microstructure and material properties of the deposit includes 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 #VI.5
MICROEN DIRECT WRITE FABRICATION OF INTEGRATED ELECTROCERAMIC DEVICES. Diane Dimes, Paul G. Klem, 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 3-D imaging, e.g., 3-D microelectronics. By cross-sectioning the solid ceramic materials with thin-layer ceramic components, it is possible to create planar devices with enhanced performance, miniaturized to the size of a few micrometers. Micron-sized components, e.g., sensor elements, rapidly-produced prototype circuits. The spray devices employed here are novel, but are essentially based on variations of reasonably well understood processes: e.g., High-Velocity Oxygen Fuel, Plasma spray, and Solvent Spray Deposition. By using spray-focused beams and collimation, we have spray-formed fine silver conductor lines having two micrometer bulk resistivity. An interesting component based on barium titanate with sprayed dielectric layers of 50 nm with resistivities of ±25 Ohm.cm has possible applications in 1KOhm/sq. Hybrid thermal spraying systems have allowed us to fabricate high temperature circuitry. 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 in 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 compounds 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 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.
defects in these multilayer structures, we have also characterized the
sintering behavior of individual layers, in constrained and unconstrained structures, 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 fabricate 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
Cristian M. Megrants, 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 nano-particle 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 5000 m/s impacting a compliant substrate. The substrate is subsequently processed at 300°C 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 10-125 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
variance of droplet electrification parameters and fluid properties,
and to appreciate the micro-physical behavior of the conductive ink as
it flows through the droplet generator.

11:00 AM V1.7
ION BEAM IN-SPORT CHEMICAL VAPOR DEPOSITION
OF DIELECTRIC MATERIALS. Heinrich Wenzel, Alois Luquet,
Helmut Langenbach, Emmerich Bergholz, Vienna University of
Technology, Institute for Solid State Electronics, Semiconductors and
Technology, Vienna, AUSTRIA; Martin Grisch, Herbert Hutter,
Vienna University of Technology, Institute for Analytical Chemistry,
Vienna, AUSTRIA.

Materials providing a deposition technology applicable in the sub-
micron range are the key factor for development of microelectronic devices. Especially, dielectric films are essential materials for generating durable reliable electric insulation. A focused ion beam tool allowing locally
confined chemical vapor deposition has been applied to direct-write
taior-made microstructures of silicon oxide 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 mechanism should lead to significantly improved
dielectric material properties. Using silicon and oxygen as
volatile precursor introduced via a nozzle system silicon oxide was
deposited at ambient temperatures on various materials such as Si,
GaAs, or metals. The deposition process was initiated by a focused
Glow Discharge at process 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 deposition in a capacitor design
performed as elementary test structures for a systematic
investigation of conductivity and breakdown voltage. The chemical composition of the layers was investigated by secondary ion mass
spectrometry (SIMS) and revealed effects of atomic mixing from both,
the substrate and the ambient. The variability 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 films of significant influence on insulting 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 dielectric
leads to improvements in electrical properties.

11:15 AM V1.8
PULSED UV LASER APPROACHES TO DIRECT WRITE
PROCESSING. David P. Taylor, Bill Hansen, Pete Fugain, Meg
Alphonse and Henry Helfen. 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 active 3D microstructures required by certain
devices. Our efforts to develop efficient processing techniques include
both laser seed templates for electrospray plating and laser exposed
techlaw glass ceramics. In both of these examples, the direct write
process employs a pulsed UV laser to make an electronic connection 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 lines at
particular points; either to increase 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. Clark, CMS
tedectronics Inc, Stillwater, OK.

Direct write in the past has generated the excitement of possibly
replacing photolithography for all electronic applications. Removing
the need to store substantially increase 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
begins to settle in, so did photolithography 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 technologies, 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.
Poulina Atmasou, Mark J. Hampsden-Smith, Toivo Koda, Klaas
Kunze, Superior Micro-Powders, 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
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. Geracek, H.J.
Rack, Clemson University, Dept. of Ceramic and Materials
Engineering, Clemson, SC; A. Piggot, R.C.Y. Auyeung, S. Lukow,
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 10mm which have both
electronic and display applications. This technique termed Matrix
Assisted Pulsed Laser Evaporation Direct Write (MAPLE DW) uses a

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high energy focussed photon source in combination with a ribbon to fabricate materials onto a range of substrates at room temperature without preheating. The work 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 (λ = 248 nm) was used, focused down to average spot sizes ranging from 10 - 200 μm with fluences ranging from 0.1 to 1.5 J/cm² at repetition rates between 1.5-50 Hz. All depositions were performed at room temperature and atmospheric pressure. In situ and ex-situ monitoring of the transferred materials was performed by both pulsed Nd:YAG laser and conventional furnace heat treatments at temperatures ranging from 200–1200°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 V.2.3 THICK FILM HIGH K DIELECTRICS FOR DIRECT WRITE ELECTRONICS. Paolina Atanasova, Mark J. Hampden-Smith, Toivo Kodis, Klaus Kozine, 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 V.2.4 ROLE OF POWDER PRODUCTION ROUTES IN DIRECT WRITE APPLICATIONS. M.B. Arun Ramsay, 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 bimetallic oxides such as ferrites are also possible from these techniques in the nanoscale to micrometer size ranges. In this presentation, an overview of the different routes used for production of metals, 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 V.2.5 THICK FILM CONDUCTOR MATERIALS FOR DIRECT WRITE ELECTRONICS. Paolina Atanasova, Mark J. Hampden-Smith, Toivo Kodis, Klaus Kozine, Superior MicroPowders LLC, Albuquerque, NM.

The fast processing rates, low conversion temperatures and low densification temperatures required for direct write processes allow electronic materials to 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 for 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 V.2.6 MATERIAL SYSTEMS USED BY MICRO DISPENSING AND INK JETTING TECHNOLOGIES. Je Zhang, Ivan Shimagin and Daniel Gamot at 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. Interest 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 inkjet 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, cost estimation for using micro dispensing technologies is conducted to compare it to current manufacturing technologies.

3:30 PM V.2.7 DIGITAL PRINTING OF LUMINESCENT MATERIALS. Mark J. Hampden-Smith, Toivo T. Kodis, Superior MicroPowders, Albuquerque, NM.

Digital printing of luminescent materials is becoming a very popular printing technology in the electronics industry. The benefits of digital printing over other printing technologies are well understood. In this presentation, we will discuss the advantages of direct writing technologies in general and digital inkjet printing in particular for producing detailed and high contrasted images with processing rates that are orders of magnitude higher than other printing techniques. The following topics will be covered: material science, inkjet inks, printheads, inkjet printing equipment, digital printing in the semiconductor industry and challenges.

3:45 PM V.2.8 DIRECT WRITE PRINTING OF POLYMER SOLUTIONS FOR HIGH RESOLUTION LITHOGRAPHY. Scott M. Miller, Anton A. Diefenbaker, Sandra M. Troim, Princeton University, Dept. of Chemical Engineering; Sigmund 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 photodecomposition 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 heterogeneous patterned surface before and after transfer to a target surface. Suitable control over the aspect ratio 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 V.2.9 SOLGEL-DERIVED (β) COMPOSITE MATERIALS FOR DIRECT-WRITE ELECTRONICS APPLICATIONS. Steve Coleman1,2, Robert Parkhill1, Robert Taylor1 and Edward Knobbe1. 1Thin Film and Materials Processing Group, Department of Chemistry, Oklahoma State University, Stillwater, OK; 2CMS Technology, Stillwater, OK.

New solgel-derived β composite ceramics are presently being developed for direct-write electronic applications. These β 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, solgel-derived β composite materials exhibit substantially reduced processing temperatures. Solgel derived systems have been shown to be compatible with the development of rapid prototyping methods and the chemistry also allows 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 solgel β composite electronics device components will be described.

4:15 PM V.2.10 CONTROLLED THERMAL DEGRADATION IN THE DESIGN OF POLYMERS FOR LITHOGRAPHIC APPLICATIONS. Stefano Vansteenkiste, Yves Martel Etienne H. Schacht, University of Gent, Dept. Organic Chemistry, Ghent, BELGIUM; Marc Van Damme, Huls van Aert, Jan Vemeersch, 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 108-joule range (80 ns or 1.04 mm), capable of ionizing and ablating materials for microsurgery 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 micromachining or patterning processes. Since the entire output beam from a DPSS laser can be focused to achieve spot sizes of 1.530 μm over large working distances, this technology eliminates the need for photo-mask and allows material modification in a direct-write fashion. Therefore, this process offers promise 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 tert-butylcarbanilide manganese tetracyanomethane. The yield and purity of the synthesized compound was monitored by dynamic contact angle measurements. Subsequently, the interaction between polymer substrates, prepared by solvent or spin coating, 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/GCMS analysis) governing the processability and the applicability of the system, were studied. The morphology of the obtained patterns (resolution, control over edge profile, 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 dichloromethane tris(dimethylaminomethylmethacrylate). This was a large-scale, high-density fabrication. It was observed that the large-pore radius change results in a positively working chemically amplified resist.

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 University 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 deposition on monocrystalline silicon substrates was formed employing thermal spray techniques. Silicon powder is injected into a high-velocity 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-V, which are the metastable phases retained after depressurization. The polycrystalline silicon coating exhibits a fine dispersion of nanocrystalline grains of the pressure quenched phase, with varying sizes and random orientation. The present work addresses experiment and theory to investigate the electrical characteristics such as 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. Hot carrier measurements have been performed and show a mobility that is not observed on the order of 50, about one order of magnitude less than typical values for single crystal silicon. The resistivity value of 1 Ω cm, when converted into impurity concentration, gives 1.0 x 10^17 atoms/cm^3 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/nanocrystal 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. Photocconductivity 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 photocconductivity. Theory and experiment will be discussed.

Acknowledgments: This work was supported by the MRSEC program of the National Science Foundation under grant no. 982570 through the Center for Thermal Spray Research.

4:45 PM V2.12
DEVELOPMENT OF NANOPARTICULATE MANGANESE DIOXIDE THIN FILMS AS NOVEL ELECTROCHEMICAL MATERIALS FOR DIRECT WHITE TECHNOLOGIES. Shih-Chen Peng, Suk-Run 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, optical, and capacitive spectroscopy over the frequency range of 10 mHz to 1 kHz. These films showed a distinctive impedance response depending upon the range of frequencies; an almost purely capacitive behavior at low frequencies, a diffusional behavior at intermediate frequencies, and a purely resistive behavior at high frequencies. These frequency responses are independent of applied dc polarization potential within the range of 0.0 V to 4.0 V versus SCE. Capacitance values of these films in various polarization conditions ranged from 2.6 mF/cm2 to 4.5 mF/cm2, with contributions from both the double-layer capacity and pseudocapacitance associated with faradic processes. While porous electrodes of nanoparticulate MnO2 materials have resulted in an increase in their utilization, the distribution 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 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 resistivity of the pore electrolyte, and by optimizing the microstructure such as the porosity, pore size distribution and film thickness. Our research work has been in its implementation to 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: Dwayne Dimos and Douglas B. Chrisney
Tuesday Morning, April 26, 2010
Salon 12/13 (Marriott)


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 the MEMS transfer (LIFT), but different in terms of the fundamental transfer mechanism and materials used. In MAPLE DW, a focused pulsed laser beam interacts with a composite target on a laser transparent support or ribbon. Ideally, the laser energy melts the particular 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 any 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, ferroelectric, ferrites, polymers, and ceramics) and to <1-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 IMMERSED ION IMPLANTATION SYSTEM WITH A PLANAR RFI PLASMA SOURCE. Linling Wu, Dennis M. Manos, College of William and Mary, Department of Applied Science, Williamsburg, VA.

A large-scale plasma source immersed ion implantation (PSI) system with plasma coil RFI plasma source has been used to study an inkless, deposition-free, maskless surface patterning as an alternative to direct writing techniques in optoelectronic systems by implantation. The apparatus has a chamber 0.61m in diameter and 0.61m tall, with a base pressure in the 10^-10torr range, making it one of the largest available PSI systems. The system uses a 0.43m diameter plasma r.f. antenna to produce dense plasma capable of
large-area, uniform materials treatment. The process causes minimal dimensional change, avoids thermal distortion of the written surface profiles and can treat non-planar 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 spectral 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 profiles and enhanced nitrogen contamination around the stoichiometry level. Measured linewidth and profiles are compared to the mask features to assess lateral diffusion, pattern transfer fidelity, and wafer-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 target is one output of these calculations. The calculation also modeled the shape and size 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/V3.3
LASER AND FOCUSED ION BEAM DIRECT-WRITE GROWTH OF 3-DIMENSIONAL MICRO- AND NANOSTRUCTURES.

Three different regimes of direct-write growth will be discussed: (1) growth of ceramics from gas phase precursor mixtures including dimethylsilylmonoxy and continuous wave/pulsed laser surface exposure in the visible resulting, with high growth rate, in complex three-dimensional aluminium oxide structures, which, of required, can be metallized with platinum using gas phase P(PPs)/4, (2) metal growth on surfaces adsorbed precursors and pulsed laser exposure with short pulses, (3) growth of metals from surface adsorbed precursors including W(CO)5 and Focused 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/V3.4
INK-JET DEPOSITION OF CERAMIC SLURRIES. N. Reis, B. Deretich, UHIST, 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 inkjet printer developed for pattern making (Sanders Modelmaker Die-PRO). Ceramic suspensions are generally more viscous than the fluids normally passed through inkjet heads. This may alter the response of the inkjet 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 inkjet printing conditions for ceramic suspensions.

10:00 AM V3.5/V3.5
LATERAL REDISTRIBUTION AND FILM PROFILES DURING INK-JET PRINTING OF POLYMER LED’S. T.R. Hehner, B. Diamond, C. Madigan, R. Regnier, S. Trojan 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 and the dissolved desired materials in one dispensable 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 distribution of organic dyes and small electron transport molecules in the final polymer film. When edge-pinching of the droplet occurs during drying, convective flows can lead to flow divergence segments 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 droplet, or by chemically bonding the molecules to a polymer backbone. Both methods have been demonstrated successfully in LED’s practice, which will be discussed.

1:30 PM V3.6/V3.6
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 in not readily available for many systems other than water. This talk will discuss the calculation of 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/V3.7
NANOTECTONIC PRINTING: DIRECT PATTERNING OF NANOPARTICLE INKS IN MICRO- AND MICRO-ELECTRO-MECHANICAL SYSTEMS. Colin Bulikasp, Sawyer Fuller, Eric Wilhelrn, Saul Griffith, Brent Ridley, Brian Hubert, Joseph Jacobson, MIT, MediaLib, Cambridge, MA.

Recently [Science, 286,746, October 22, 1999] we demonstrated an all-organic 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/V3.8
RAPID PROTOTYPING OF PATTERNED FUNCTIONAL NANO-STRUCTURES. C. Jeffrey Brinker, Hongqing Fu, Youfeng Lu, Dhan Doshi, Nicola Hawing 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 the preparation of hybrid, organic-functionalized silica frameworks as well as metallic and (organic) polysilicon nanocomposite films and particles. Then we will discuss new results where we utilize these homogeneous silica/surfactant solutions as inks in a variety of rapid prototyping processes like microemulsion lithography, inkjet 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, macroporous pores are organized into 1-, 2-, or 3-dimensional networks, providing non-selective accessibility from the gas and liquid phase, and on the microscale, 3-dimensional arrays and fluidic or photonic systems may be defined. Finally by introduction of photoactive molecules into the inks, we can write arbitrary patterns of photoactive 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/V3.9
RAPID FABRICATION OF PATTERNED FUNCTIONAL NANOSTRUCTURES VIA DIRECT WRITING AND PRINTING. Hongqing Fu, Youfeng Lu, Scott T. Reed, Todd Beauch, 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
structures and functionality in photoactive thin film silica mesophases. Bhim A. Doshi, Nicolas Haas, Richard Cook, Hongyou Fan, Jeong-Hoon Lee, and H. Carl
department of Chemistry and Chemical Engineering, University of New Mexico, Albuquerque, NM. 2 Vienna University of Technology, Vienna, AUSTRIA. 3 Sundog 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 hierarchical nanostructures. Thin films are one of the most promising applications of so-called mesoscale structured materials, and the ability to build hierarchical structures and functionality is the key to their successful implementation in future microelectronics. Recently, so-called micro-contact printing (µCP) and micro-molding in capillaries (MMIC) techniques have been used to create patterned thin film silica mesophases. Here we report a novel lithographic approach 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 photoreactive generator in the casting sol. Dip/Apil coming results in the formation of a photoreactive mesostructured thin film. Selective UV exposure, which can be achieved using a mask or via direct laser writing, results in localized photoreactive 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, M/S-NIR and atomic force microscopy. Our ability to spatially control structure and functionality is of interest for sensor arrays, nano-protectors, 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. Tomas, Princeton University, Dept. of Chemical Engineering; Sigurd Wignler, Princeton University, Dept. of Electrical Engineering, Princeton, NJ.

Using a combination of experiment and simulation, 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-solid surface profiles, as well as the effect of chemical and topological defects. Comparison of the computed shapes with glycerol microdroplets on a patterned silica 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 micro lithography of signification to the fabrication of semiconductor devices, optical diffusion elements or fluid microchannels.

2:30 PM V4.4

Nanostructure electron beam patterning using titanium isoproxide films. William Mitchell, University of California, Dept. of Electrical and Computer Engineering, Santa Barbara, CA. Evelyn Hsu, 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 thin film of silicon dioxide provides the industry with a tool that can be used to provide an intrinsic level of flexibility in the production of a wide variety of "nano-sensitive" structures, e.g., structures that utilize quantum wire and dot arrays. We have previously shown that a thick, multilayer film of titanium isoproxide condensed on a cold substrate exhibits excellent intrinsic properties; it is iUV compatible, low electron doses (order of 1000's of µC/cm²) convert the volatile precursor to a nonvolatile oxide deposit, and the deposited oxide is resistant to etch attack. We have recently measured substrate temperatures (350 °C) in this work, and have used Auger electron spectroscopy and scanning electron microscopy to study the structure of the deposited films.
investigate the spatial resolution capability of these condensed titanium nitride layers on a gold (-20°C) GaAs substrate. We have found that both resolution and sensitivity depend on the initial multilayer film thickness. The optimum condition determined with our experimental configuration resulted in a dot size of approximately 0.1 μm by exposing a film 20 nm in thickness to an electron energy of 0.1 eV. However, dots of 1 μm thick were inefficient resistors and required a large electron beam dose (>10 pC/pixel) to effectively observable deposition.

Moreover, the produced dots were rough and poorly defined (with sizes on the order of 1 μm). Although such a resolution is sufficient to investigate, i.e., dot sizes >1 μm. Possible origins of the observed behavior, in terms of electron backscattering and secondary electron emission, will be discussed.


2:45 PM V4.5

MICROFLON DIRECT WRITE FABRICATION OF MULTILAYER CAPACITORS AND INTEGRATED PASSIVES. P.G. Clem, B.A. Tuttle, P. Yang, N.S. Bell and D.D. Dimos, Sandia National Laboratories, Albuquerque, NM; G.L. Brenecky, 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 towards combination of multilayer LTCC and sub-μm 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 gives high integration of single and multilayer capacitors of high dielectric constant (K > 1000) X7R BFeCo thick films and electrodes. Specifics of shunt development and microstructural and stress evolution will be discussed. Approaches to low temperature preparation of the dielectric and RF dielectrics and use of Microcon 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-AC04-94AL85000.

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 contracting areas of microprocessors and microelectromechanical systems (MEMS). Recent trends in microelectronics, including the dramatic recent shift to flip-chip electronic packages, have been driven in part by significant part by solutions provided by the laser direct writing technology. Similarly, laser microchemical direct writing provides best solutions for some instances where laser direct writing can be used.

We will review the microcavities 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. Tanya Cak, C.M. Hong, Sandra Deais, Sigurd Wagner, Princeton University, Dept. of Electrical Engineering, Department of Electrical Engineering, Princeton, NJ.

We have developed a technique for the jet printing of copper lines using solutions of a metallic organic precursor, copper hexamethylenetetramine. An 80-μm wide jet printed liquid line is observed to split into two 20-μm wide lines, which can be converted to copper lines of >10-μm diameter by a 20°C process. We observe further splitting into four parallel lines, both in redox results with written lines of copper hexamethylenetetramine solution in chloroform. The position and widths of the double or quadruple lines of copper hexamethylenetetramine are symmetric of the axis of the liquid jet.

The jet spraying 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, vapor rate, contact angle and viscosity as functions of the solution concentration. The data make evident that the Marnagoni 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 Marnagoni number changing by an order of magnitude over our concentration range. The existence of this change in the Marnagoni 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 of the solution and this phase transition determines. 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. Cho, 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 hexamethylenetetramine onto a glass substrate. This layer is imprinted with a mold to form lines with width and spacing down to 1 μm. The molding is made possible by the soap-like flow of the copper hexamethylenetetramine. These lines then are converted to metallic copper in two steps. In the first step the copper hexamethylenetetramine 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 300°C in a mixture of hydrogen and nitrogen. Optical micrographs and atomic force micrograph/profiles show clearly resolved lines of the precursor copper hexamethylenetetramine. The lines of converted copper metal are sharper and thinner than those of the precursor. Their grain size, determined from line width, is ~40 nm. The resistivity of the copper lines is 8 μΩcm. Thus the imprinting of a copper organic precursor provides a route for the direct patterning of high-resolution low-resistance copper conductors.

4:15 PM V4.9

NANOPARTICLE-BASED DIRECT WRITE METALIZATIONS FOR PHOTOVOLTAIC DEVICES. David Jinley, Calvin Curtis, Doug Shah, 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 high resolution (>10 μm) contacts lends itself well to the application of nanoparticle based inks. We will discuss recent results on the application of such inks for metalizations in photovoltaic cells and microelectronics. Metal powders were generated by the electroexplosion of wire process both in Russia and in the US. Ink was prepared from Ag, Cu and Au. In some cases surface oxide was removed chemically and the surface stabilized through the application of stabilizing layers. Direct Writing approaches were considered for large area metalizations and patterned metalizations. 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 than 100 μm 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 Technologies, Inc., Stillwater, OK; James Caher, 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 increases the physical dimensions of the supporting antenna decrease. This makes the fabrication of these antennas difficult. Several designs, which may be considered high performing antennas, are difficult to reproduce and many times cannot be fabricated at all due to the sophistication of the tooling and precision necessary for success. A combination of Laser Chemical Vapor Deposition (LCVD) and Laser Sintering (LS) of powders 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 taken in the fabrication of the devices. 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. Hoffman, 1, U. Utke, 1, B. Devi, 2, K. Leifer, 2, F. Ciccioni, 2, P. Doppelt, 2, E. Kupich, 2, Microengineering and 2Physics Departments, Swiss Federal Institute of Technology Lausanne, EPFL, 1Ecole 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 $100$ SEM with tungsten filament, operating at $25$kV. Typical beam diameter is $20$ nm at $4$Pa probe current, $800$ nm at $8$nm maximum current. The SEM is controlled by a NIST Systems NPGS software running on a PC. The specimen chamber background pressure is $2 \times 10^{-4}$ 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 $3 \times 10^{-4}$ mbar. The substrate holder and internal reservoir could be independently heated or cooled in the range of $0$ - $150^\circ$C. As substrates we used mostly $\text{SiO}_2$, coated $\text{Si}$ wafers, with $\text{Au}$ electrodes for resistivity measurement. Metal containing lines were deposited using the carbon-free [RhCl(PF$_3$)$_2$]$_2$ as precursor for EBID. The measured vapor pressure of the precursor at room temperature is $7 \times 10^{-12}$ mbar$^2$. TEM images allow the determination of the metal cluster size that deposits on the electron beam current used to induce the deposition. Auger electron analysis shows that the deposited lines contain about $40$% Rh. When $\text{PF}_5\text{AuCl}$ as precursor, deposition resulted in highly conducting lines with electron beam currents as low as $0.01$ nA. Resolution of the gold clusters during deposition is shown by ex-situ TEM studies.


SESSION V5/S4: JOINT SESSION: LASER DIRECT WRITING
Chair Herbert Herman
Wednesday, April 26, 2000
Nob Hill C/D (Marriott)

NOTE EARLY START

4:30 AM VS5/4


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 ($\sim 200$ C) and short times ($\leq 10$ ns). As a result, new colloidul and molecular materials must be developed to meet these conditions. Optoele 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 on laser-induced 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 resistivity values of $10$ ohm bulk. Likewise, single phase, binary titanium has been densified at low temperature processing. Deposition has been demonstrated on a wide range of substrates including alumina, glass, polycrystalline barium titanate, PVC plastic, and various metals.

9:00 AM V5/3/4

LASER INDUCED ETCHING OF $\text{Si}$ WITH $\text{F}_3\text{Si}$ USING CuBr. B. Temesc, 1 M. P. Tarnov, 1, M. P. Tarnov, 2, L. Zumbach, 3 Dept. of Semiconductor Materials, University of Chemical Technology and Metallurgy, Sofia, BULGARIA. 2Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Science, Sofia, BULGARIA.

Laser induced etching of $\text{Si}$ with $\text{F}_3\text{Si}$ was 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 of $4-10$ W with repetition rate of $20$ kHz and the pulse duration of $60$ ns. $\text{F}_3\text{Si}$ was used at the partial pressure in the range of $0.1-1000$ mtorr. The basic processes parameters were varied in the ranges: scanning speed from $5$ to $100$ ($\mu$m/s) and substrate temperature of $100$ and $400^\circ$C, respectively. The etched substrates were investigated by Scanning Electron Microscopy (SEM). The influence of the process parameters - laser power, scanning speed, $\text{F}_3\text{Si}$ pressure and background temperature of the depth and width of etched groves was studied. The etched rates were in the range of $0.5$ - $25$ $\mu$m/s.

9:15 AM V5/4/4

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. First, these excimer lamps offer narrow-band radiation at various wavelengths from $108$ - $354$nm and over large areas. Since excimer lamps have no stable ground states self-absorption of the emitted radiation is almost negligible. As a consequence, 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 and silicon oxynitride layers were the main target 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 (titanium oxide, tantalum, or PZT) and low dielectric constant (polymide and porous silica) thin films by photo-CVD and solgel processing, as well as the effect of low temperature UV annealing, are discussed. Films 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/cm$^2$ and $32$ pA/cm$^2$ have been obtained for the m-grown titanium oxide films formed by photo-induced processing and photo-CVD, respectively, several orders of magnitude lower than for other m-grown films prepared by any other technique. A subsequent low temperature $40^\circ$C UV annealing step improves these to $2\mu$A/cm$^2$ at $0.5$MV/cm and $7\mu$A/cm$^2$ at $40^\circ$C, respectively. These values are essentially identical to those only previously obtained for films deposited by alternative methods and annealed at temperatures between $600$ and $1000^\circ$C. These 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.
LASER DIRECT WRITE OF CONDUCTING AND INSULATING TRACES ON CARBIDE: A Novel Method for Laser Direct Writing Mesoscopic Conformal Electronic Devices and Sensors


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 or 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 200-μm-thick wafer with a single side coated with a powder and/or a metal organic precursor of interest (metals, ferrites, ferromagnetic, 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 (1 = 348 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 10-20 Hz. Glass, aluminum, duralont 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:YLF laser (1e-1.66 microns) and conventional furnace heat treatments at 250°C to increase the substrate adhesion and to transform the metal oxide while removing the organic precursor material. Chemical composition and In-situ characterizations was performed by XRD and XPS. Characterization was performed by scanning electron microscopy and 3D surface profilometry. Electrical characteristics was performed with a HP 4291B Impedance Analyzer.


ParMD 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 directly 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 photo-mechanical photolithographic technology. Recently the ParMD 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 usable electronic properties, particularly of resistors and capacitors, the electrical properties of all these novel materials could be improved by laser processing. This paper discusses preliminary results on laser processing of ParMD conductors and components in two different systems.

LASER SIMULATION OF SUBSTRATE HEATING FOR DIRECT WRITE OF MESOSCOPIC INTEGRATED CONFORMAL ELECTRONIC DEVICES (MICE).

Sean Loyar, Sandi Mummert, J.C. Sheu, CF Prism, 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 combines Monte Carlo and Direct Optimize 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 incorporates the 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 results.
validation. The capabilities, limitations, and potential applications of the model with respect to MICE are discussed.

11:45 AM V5.11/J4.11


As the trend towards device miniaturization 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 oxidizing 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.