SYMPOSIUM J
Laser-Solid Interactions for Materials Processing
April 25 – 27, 2000

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*Invited paper
SESSION J1: FUNDAMENTALS OF LASER DEPOSITION AND ABLATION
Chairs: David P. Norton and Tom Dickinson
Tuesday Morning, April 25, 2000
Nob Hill C/D (Marriott)

8:30 AM *J1.1
WHEN A MILD MANNERS 1.5-µV PHOTON MEETS A BIG 10 ev BANDGAP: WHAT HAPPENS? STUDIES OF LASER DEPOSITION FROM MODIFIED SURFACES OF IONIC SINGLE CRYSTALS
Tom Dickinson, Washington State University, Dept. of Physics, Pullman, WA.

Wide bandgap insulators such as ionic crystals are highly transparent to most laser light. Nevertheless, at very low laser intensities we show evidence of strong interaction 1. We present recent experimental results on the physics and chemistry of laser induced desorption and emission of atoms, ions, and electrons from single crystal inorganic crystals. The influence of defects generated by surface modification is shown to dominate these low laser fluence emission processes. The consequences of electron beam irradiation, irradiation by two laser wavelengths, and mechanical treatment of these ionic crystal surfaces are presented, showing dramatic enhancements in emission intensities, often with significant morphological changes. Physical models of these effects will be presented and the implications regarding material removal rates, plasma formation, and chemical analysis will be presented.

9:00 AM J1.2
ANGLE RESOLVED CHARGE COLLECTION MEASUREMENT FROM UV AND VISIBLE LASER ABLATION OF GRAPHITE: GROWTH FRONT PROFILES
Paul T. Murray, Research Institute, University of Dayton, Dayton, OH.

The purpose of this study was to investigate the interaction of high-power laser radiation with graphite and to determine the wavelength dependence on ejection dynamics of laser plumes. The target was ablated by two different laser radiation (λ = 355 and 266 nm). Angular dependencies of intensity and velocity of the charged particles were obtained by Friedel cut measurement at various laser power densities. The most probable speed of the charged particles from the UV laser ablation was less than that of from the visible laser ablation but the distribution function of the charged particles from UV ablation shows less angular dependence than that of from the visible laser ablation. The reasons for these differences will be discussed.

9:15 AM J1.3
LASER ABLATION OF SOLID OZONE: Hidetaka Nomura, Tetsuya Nishiguchi, Yoshiki Morikawa, Masaharu Miyamoto, Shingo Ichimura, Electrotechnical Laboratory, Tsukuba, JAPAN.

Ablated species from solid ozone by a UV laser have been investigated using time of flight method through a quadrupole mass filter. The results show that the main ablated species of solid ozone can produce a neutral ozone beam with a translational energy which is far above that of room temperature. High concentration ozone from an ozone jet generator is solidified on a sample substrate attached to a copper block which is cooled to 30 K on a cryopump. The purity of the solid ozone is further improved by raising the substrate temperature above the boiling point of oxygen, a major impurity. Pulsed laser light from a KrF laser (248 nm) which hits the Hartley band of ozone lying from 300 nm to 300 nm with a minimum at ca. 250 nm is used to ablate the solid ozone. The ablated species are a mixture of ozone and molecular oxygen as well as atomic oxygen. The ratio of ozone against molecular oxygen in the mixture increases as the substrate temperature during the ablation is set higher, but the highest ratio is just above 20% at 60K. The total amount of the ablated ozone becomes greater as the power density of the ablation laser increases up to 25 mJ/cm2 and then it decreases probably because of decomposition of ozone. Gaussian fitting of the time of flight signal of the ablated ozone results in the thermal velocity of more than 1,000K. The velocity also depends on the power density of the ablation reaching to 2,000K at the highest power density available in the present experiment.

10:00 AM *J1.4
RECENT PROGRESS ON LASER SURFACE CLEANING, Y.E. Lo, W.D. Shi, M.H. Hong and W.Y. Zheng, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, Singapore, SINGAPORE

Laser cleaning as a new cleaning technique has emerged in order to effectively remove contaminants from solid surfaces. Two types of laser cleaning techniques have been developed recently, relying on pulsed laser heating of the surface without or with the presence of a thin liquid coating. Laser cleaning was demonstrated both theoretically and experimentally to be an effective cleaning technique for removing contaminants from solid surfaces without using a thin liquid layer by taking Van der Waals force, capillary force, cleaning force, and chemical bonding into account. The models not only explain the influence of incident direction, wavelength, fluence on cleaning efficiency but also predict the cleaning threshold. The experimental results show that the laser cleaning efficiency increases with increasing fluence and pulse number, but does not depend on the repetition rate. The surface cleanliness can be monitored in real time by acousto-optic and optical means. Applications of laser cleaning to clean magnetic slider surface, magnetic media surface, silicon wafer and IC mold surface will also be addressed.

10:30 AM *J1.5
LOCALIZED EXCIMER LASER ENERGIZATION MODULATION IN THE CRYSTALLIZATION OF POLY-SI FILM ON STEPPED SUBSTRATE: Yoo-Chan Park, Cheol-Min Park, Woo-Jin Nam and Min-Koo Han, Seoul National Univ, School of Electrical Engineering, Seoul, KOREA.

Excimer laser annealed polycrystalline silicon thick film transistor (poly-Si TFT) has drawn much attention for the possibility of integrating driving circuit and pixel switching devices on a low cost glass substrate. Various methods such as artificial grain seed formation and amorphous silicon (a-Si) membrane on a large area substrate have been investigated in order to increase the poly-Si grain size. The purpose of our work is to report a new laser annealing method for a-Si film crystallization employing stepped substrate. The proposed method is so simple that it does not require additional complicated process steps. Excimer laser beam irradiated on the stepped substrate which was fabricated by 5000A deep trench etch, has locally modulated energy distribution because the vertical wall of the trench is exposed to relatively lower laser energy than horizontal substrate surface. Then the a-Si deposited on horizontal plane melts by the laser energy while the a-Si deposited on vertical plane does not melt. Therefore laser irradiated silicon film has lateral temperature gradient and silicon grains are melted to grow laterally from relatively lower-temperature a-Si region into higher-temperature liquid silicon region. In our experiments, 1 µm thick buffer oxide was deposited on silicon wafer and 5000A deep trench of gate electrode pattern of the oxide. Then film deposition was performed by PECVD at 320°C on the patterned oxide substrate and XeCl excimer laser was irradiated on the a-Si film with and without capping oxide. The thickness of capping oxide was varied from 1000Å to 5000Å and the substrate temperature was varied from room temperature to 300°C. Poly-Si grain structure was investigated by transmission electron microscopy (TEM) and very large poly-Si grains of over 1 µm long and with very low defect density were obtained. This is due to the fact that undesirable radiation was suppressed because the temperature gradient in the morden silicon layer promoted lateral grain growth. In addition, it was remained as deposited on the lowest-temperature vertical trench wall. The remaining a-Si region can be used as an offset between the large grain of TPT to suppress large leakage current of poly-Si TFT.

10:45 AM J1.6
SIMULATION OF POLYCRYSTALLINE SILICON GROWTH BY PULSED EXCIMER LASER ANNEALING: Daisi Ichishima, Sumitomo Heavy Industries Ltd, Research & Development Center, Hiratsuka, JAPAN; Cheng-Guo Jin, TIC Corporation, ACT Center, Yokohama, JAPAN

Pulsed excimer laser melting and regrowth of Si films is by far the most attractive technology for fabricating poly-Si TFTs on glass surface 1. The kinetic numerical simulation is very important, not only for understanding of physical process but also for directive function in actual growth control. In conventional model, a nucleus position is given as an initial value, and then the growth process from the nucleus is analyzed. Based on the homogeneous nucleation theory 2, Ichishima et al. introduced the creation and annihilation process of nuclei into the simulation of poly-Si growth by laser annealing 3. Using the Ichishima model, we calculated the variation of average grain size on laser energy density in the case of single-pulse irradiation. The kinetic simulation model and the simulation results reproduced the super lateral growth (SLG) phenomenon observed experimentally in the near-complete melting region 4. Under the strong fluctuation of Si grain size on energy density in the near-complete melting region, it is difficult to control the actual poly-Si growth process. Through the results of the single-pulse irradiation, we turned our attention to dual-beam irradiation, where the first pulse was used to melt completely a-Si film and the delayed second pulse to control the nuclei density and the
growth. And we simulated the poly-Si growth by dual-beam irradiation. In this paper we will discuss the problem of practical use, that is, the influence of ion beam energy fluctuation and beam shape. 1) T. Sameshima, S. Usui and M. Sekiya, IEEE Electron Device Lett. 7 (1986) 276. 2) D.H. Lowndes and R.F. Wood, 2. Jam. 30 (1985) 2356. 3) D. Ishizuka et al., to be published. 4) J.S. Im, H.J. Kim and M.O. Thompson, Appl. Phys. Lett. 63 (1993) 1969.

11:00 AM • 31.7
FABRICATION AND PATTERNING OF LARGE FREE-STANDING GaN SUBSTRATES BY LASER-INDUCED LIFTOFF.
Oliver Ambacher, Mike Kelly, Claudia Miskys, Lutz Hoppel, Christoph Neubig and Martin Stutzmann, Walter Schottky Institute, TU-Munich, GERMANY.

Due to the lack of native nitride substrates, films of GaN and related nitride compounds are commonly grown on sapphire or silicon carbide wafers. Use of these substrates limits the quality and function of the semiconductor. Numerous threading dislocations are generated in the epitaxial film to accommodate the large lattice mismatch between GaN and substrate. The thermal expansion coefficients of the epitaxial film and substrate materials differ, causing stress and bowing upon cooling from the growth temperature. The use of substrate and silicon carbide substrate also complicates processing steps, such as etching, cleavage and edge facets for laser diodes and electrical backside contacts necessary for vertical optical and electrical devices. The tunnelling of excitons is low. By removing the GaN epitaxial film from the substrate using selective wet etch or reactive ion etch techniques, the GaN layer is thinned to a thickness of 500 to 1000 nanometers, suitable to thermally decompose a thin layer of GaN at the film-substrate interface. Subsequently scanned pulses of 5 ns duration with a 7 nA beam diameter were employed and the liftoff was performed at elevated temperature of 600 C to relieve postgrowth bowing. The surface of the free standing GaN substrates were polished with chemical and mechanical methods and coated with a 50 nm thick Mo/Cr layer. By this procedure epitaxial free standing substrates are fabricated with low dislocation densities and a surface roughness of 0.2 nm, suitable for homoepitaxial growth, cleaving and backside contacts. In addition to the fabrication process of free standing GaN substrates we will present the removal of GaN based light emitting diodes and transistors by laser induced liftoff and discuss recent results of the patterning of GaN layers to obtain low reflectivity surfaces or gratings for distributed feedback lasers.

11:30 AM • 31.8
THERMOMECHANICAL ANALYSIS OF THE LASER LIFT-OFF PROCESS FOR SEPARATING EPITAXIAL GaN FILMS FROM THEIR SAPPHIRE GROWTH SUBSTRATES. William S. Weng, Alberto Salles and Tim Sands, University of California, Department of Materials Science and Engineering, Berkeley, CA; Nathan W. Cheung, University of California, Department of Electrical Engineering and Computer Sciences, Berkeley, CA; Michael Kneissl, David P. Bour, Ping Mei, Linda T. Romano and Noble M. Johnson, Xerox Palo Alto Research Center, Electronic Materials Laboratory, Palo Alto, CA.

The many advances in GaN epitaxial growth have resulted in high-quality GaN material on sapphire substrates. Despite the recent improvements in GaN thin film quality, the substrate substrate still inhibits light-emitting diode (LED), laser diode (LD) and transistor device performance due to its poor thermal and electrical conductivity. In order to alleviate the substrate substrate constraint, a new non-contact technique, laser-induced lift-off (LLO), has been developed. This LLO process involves the local heating of the GaN/sapphire substrate interface in order to decompose the GaN. The transient heating of the GaN at the interface results in a rapid temperature rise and expansion of the GaN material, causing thermomechanical stress to develop in the film. The calculated stress distribution and temporal evolution of temperature and stress during laser irradiation will be presented. A finite element analysis for irradiation of a GaN surface using a KrF (248 nm, 35 ns) pulsed excimer laser showed that a fluence of 400 mJ/cm^2 is raised to the GaN surface temperature to the decomposition temperature of ~1000°C. Examination of the GaN surface morphology by scanning electron microscopy for laser times between 250 fs to 350 ps confirms the decomposition of GaN at fluences > 400 mJ/cm^2. For the LLO process, a 600 mJ/cm^2 laser fluence was calculated to decompose the GaN at the GaN/sapphire interface. This temperature rise is localized to within 20 nm of the GaN/sapphire interface. The calculated thermomechanical stress developed during the laser processing was ~ 8 GPa. Experimental results will show that mechanical fracture due to the relatively high compressive stress can be prevented using wafer thinning techniques and stiffener layers. It will be shown that the combination of LLO and wafer bonding can successfully transfer GaN thin films from sapphire onto Si, GaAs, or polymer substrates without degradation to the GaN thin film quality. In this manner, free-standing GaN thin film membranes have been fabricated using LLO without degradation of the device performance.

11:45 AM • 31.9
LASER DAMAGE IN EPITAXIAL Pb(Zr,Ti)O_3 THIN FILMS AND RELATED OXIDES PRODUCED BY EXCIMER LASER LIFTOFF.
I. Taskin, I. D. and T. Sands, University of California, Dept. of Materials Science & Mineral Engineering, Berkeley, CA.

We recently demonstrated transfer of epitaxial Pb(Zr,Ti)O_3 (PZT)-based thin films and heterostructures to virtually any substrate utilizing a novel excimer laser lift-off process, thus allowing significant flexibility in heterogeneous materials integration of oxide films for Microelectromechanical Systems and ferroelectric memory applications. The process takes advantage of the interfacial bandgap discontinuity produced by depositing high quality epitaxial PZT films onto uv-transparent MgO or sapphire substrates to separate the films from the growth substrate by application of a 250 nm excimer laser pulse (~ 38 ns) through the backside of the growth substrate. Therefore, the process relies on the difference in the bandgap energies between the oxide film and the semiconductor substrates under conventional conditions compared to conventional laser processing of exposed surfaces. Calculation of the absorption length and thermal diffusion length in PZT films shows a ~25 nm and ~125 nm, respectively. An analysis of the laser lift-off process for PZT reveals that the temperature attained at the interface for a 400 mJ/cm^2 laser pulse is ~1500°C (after 38 ns), and at ~200 nm into the PZT the temperature is ~350 °C (after 38 ns). Since the equilibrium melting temperatures are ~1200 °C, it is expected that a thin (~100 nm) liquid layer will form during application of the laser pulse, as is evidenced by observation of a quenched liquid phase by Scanning Electron Microscopy. However, measurement of the ferroelectrical properties after removal of the quenched liquid layer by ion milling show the dielectric constant and loss tangent are reduced after liftoff, from 1300 to 700 and from 0.076 to 0.035, respectively. Materials characterization of the laser damage using Transmission Electron Microscopy, Atomic Force Microscopy, Auger Electron Spectroscopy, and Rutherford Backscattering, in order to correlate changes in the microstructure and composition of the film with the observed electrical properties, will be discussed.

SESSION J2: LASER-DRIVEN NANOPARTICLE FORMATION
Chair: Kenji Ebihara and Rajiv K. Singh
Tuesday afternoon, April 25, 2000
Nobel Hill C/D (Marriott)

1:30 PM • 42.1
IMAGING AND SPECTROSCOPY OF LASER ABLATED CARBON PLUMES FOR THIN FILM DEPOSITION AND NANOCUBE SYNTHESIS. A.A. Purzycki, Department of Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN; D.B. Gheggen, X. Fan, S.J. Penkooock and G.E. Jellison, Jr., Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Imaging and spectroscopic investigations of laser ablation carbon plumes will be presented to evaluate two important application areas: 1) deposition of diamond-like carbon films and 2) carbon nanocube synthesis. 1. Deposition of diamond-like carbon. We have observed during deposition of amorphous diamond-like films in vacuum reveal intraplane gas dynamics which affect the quality of the deposited amorphous diamond-like carbon thin films. To understand these dynamics gated ICCD photography, emission and absorption spectroscopy, ion probe measurements, and laser induced fluorescence (LIF) were used. It was found that the three-component plume dynamics, kinetic energy and composition of the carbon species strongly depend on laser wavelength used for ablation (~248 nm or ~193 nm). It was shown that effective photodecomposition of the initial ejecta (C_2 to C_6) into the fast (~100 eV) C^+ ions and redeposition of the residual molecular species back to a target due to strong gas dynamic interaction within the plume are the key factors for high quality film deposition. Amorphous diamond film properties were characterized by spectroscopic ellipsometry. 2. Time-resolved imaging and spectroscopic measurements of the graphite/metal catalyzed ablation plume were performed to understand how the hot laser
plasma of initial ejecta (containing C, C2, C3, and metal catalyst atoms) is influenced by the high-pressure background gas (500 Torr Ar) at the conditions favorable for laser ablation of single wall carbon nanotubes (SWNT). The catalyst-cluster and carbon-cluster nucleation times and transport processes of the C/Co/Ni plume within the time range 20 ns at 5 s were measured using LIF and laser induced blackbody emission imaging and spectroscopy. Raw data collected from different positions in the chamber for correlation with the in situ imaging was characterized by TEM. This research was sponsored by the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy, under contract DE-AC05-96OR22464.

2:00 PM 12.2
IN SITU OBSERVATION OF NANO PARTICLE FORMATION AND GROWTH DURING LASER ABLATION K.S. Seol, Y. Okada, K. Takeuchi, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, JAPAN; J.P. Conner, Institute of Physics, University of Sao Paulo, Sao Paulo, BRAZIL

Nanoparticle formation by the interaction of intense laser beams with solid surfaces is a common phenomenon. Although widely observed in experiments of laser induced film growth, few studies have concentrated on the dynamic behavior of these nanoparticles in the gas phase, i.e., prior to deposition. This is because there are few techniques capable of performing direct in situ measurements on gas-augmented nanoparticles. In this work we have used lowpressure differential mobility analysis to perform high-resolution particle spectrometry in the 1-200 nm size range and study the gasphase dynamics of the in situ formed clustered YAG laser ablation of a silicon target in pure gas atmosphere. Background pressures in the 70-400 Torr range and laser fluences between 0.1 and 1.0 J/cm² were considered. In situ measurements reveal that the nanoparticle spectrum is described by bimodal size distributions with a concentration peak in the 5-10 nm size regime and another around 200 nm. Transmission electron microscopy on deposited nanoparticles shows that the large 200 nm objects are fractal-like conglomerates formed by collisions of the small 5-10 nm particles. At low pressures (< 150 Torr) and low laser fluences (< 0.2 J/cm²), the nanoparticle spectrum is dominated by the 5-10 nm nanoparticles. For a laser fluence of 0.2 J/cm², for example, the mean diameter of these small particles changes from 4.5 nm at 150 Torr, to 70 nm at 700 Torr, while their peak concentration drops from 10⁸ to 10⁶ cm⁻³ in the same pressure interval. Within the framework of the aerosol general dynamic equation, this pressure dependence suggests a particle growth by Brownian coagulation, as the particle size scales with the system residence time. For laser fluences above 0.8 J/cm² a surge of particles with sizes around 200 nm is observed. This leads to the depletion of small particles and large conglomerates become the predominant objects in the gas-augmented population.

2:15 PM 12.3
DEPOSITION OF NANOTUBES AND NANO TUBE COMPOSITES USING MATRIX-ASSISTED PULSED LASER DEPOSITION. P.K. Wu, Department of Physics, Southern Oregon Univ., Ashland OR; J. Fez-Queral, A. Pique, D.B. Chrisey and R.A. McNeill, Naval Research Laboratory, Washington, DC.

Using the Matrix-Assisted Pulsed Laser Deposition (MAPLE) process developed at the Naval Research Laboratory, nanotubes and nanotube composite thin films are successfully fabricated. This process involves dissolving carbon nanotubes in a suitable solvent, evaporating the mixture to form a solid target and using a pulsed laser to evaporate the target for deposition inside a vacuum system. The volatile solvent is pumped away leaving the film material on the substrate. Using this technique, we are able to transfer single wall nanotubes (SWN) from the target to the substrate. The SWN sustain no observable damage during the deposition process. Using SWN and polymers as the target material, SWN/polystyrene and SWN/polyethylene composite films were made. SEM micrographs show that SWN were imbedded in the polymer matrix. Using a simple contact mask, these composite thin films can be patterned down to 20 nm thick lines. This technique is especially useful in the fabrication of a variety of substrates, i.e., Si, glass, plastic, and metal, using the same target and deposition conditions. Because material properties of polymers, such as dielectric constant and strength, can be altered by the incorporation of SWNS, composite of superior quality can be fabricated by MAPLE for protective coatings, electronics, and biomedical applications.

3:00 PM 13.4
NOVEL NANOCRYSTALLINE METAL SEMICONDUCTOR COMPOSITES BY PULSED LASER DEPOSITION. J. Narayan, NSF Center and Dept of Materials Science & Engineering, Raleigh, NC.

We have used pulsed laser deposition to fabricate nanocrystalline thin film composites, where size of nanocrystals has been controlled by nucleation and growth of three-dimensional islands via a self-nucleation synthesis process. Properties of interfacial regions, which are crucial in mechanical properties of thin film composites, can be controlled by appropriate alloying. Thus, we have fabricated superhard thin film nanocrystalline composites of copper and zinc. We present a model of hardness vs. grain size that explains the mechanical properties over the entire range. A similar approach has been adopted to fabricate semiconductor (Ge, ZnO) nanocrystallites embedded in larger bandgap materials such as AlN and α-Al₂O₃. The quantum confinement of carriers is achieved in a controlled way, and different wavelength of luminescence has been achieved from a single multilayer structure. Novel properties and applications resulting these metal and nanocrystalline composites will be discussed.

3:30 PM 12.5
SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE NS-ALUMINIDES BY LASER ABLATION TECHNIQUE. Takashi Yamamoto, Aoyi Maumander, Univ of Illinois, Dept of Materials Science and Engineering, Urbana, IL and Dept of Mechanical Engineering and Applied Mechanics, Univ of Michigan, Ann Arbor, MI.

Nanocrystalline Nb-aluminides have been synthesized by laser ablation by varying the processing variables such as laser energy density and ambient He gas pressure. Ablation rate of the target material is relatively insensitive to the variation of He gas pressure. However, it was observed that there is a threshold laser energy density, above which the ablation rate does not increase. Yield of nanocrystalline material, as measured from XRD pattern peaks on the 040 plane, was found to vary strongly on the He gas pressure. No nanocrystalline material was formed at 0.1 Torr and the collection rate peaks near 1.0 Torr at all laser energy densities. The mean diameter of the nanocrystalline particles is 5 to 13 nm depending on the processing condition. Transmission electron microscopy reveals that the majority of particles is identified as NbAl₃ (D₀₅) type. Energy dispersive spectroscopy (EDS) revealed that atomic ratio of Al/Nb decreases from the stoichiometric composition of NbAl₃ with increasing laser energy density and decreasing backing gas pressure. High-resolution electron microscopy (HRTEM) reveals the atomic structure of the NbAl₃ particle of the D₀₅ type at all the processing conditions. NbAl₃ particles of the D₀₅ type crystal structure are identified at lower gas pressure and higher laser energy. X-ray diffraction reveal that the yield of particles of small and large sizes are observed in the same time and the volume ratio of the two distributions is in between 0.7 and 1.1. Formation mechanisms of the nanocrystalline powders is proposed in view of the structure-processing relationships.

3:45 PM 12.6
SYNTHETES AND CHARACTERIZATION OF INDUM NITRIDE PARTICLES THROUGH REACTIVE LASER ABLATION. Amith Murthy, Valerie Lepert, Ian Kennedy, Subhash Rabad, University of California at Davis, Dept of Chemical Engineering and Materials Science, Davis, CA.

Indium nitride (InN) was synthesized by pulsed laser ablation of a pure indium metal [99.999%] target in flowing high purity nitrogen atmosphere. The nitrogen pressure was maintained at ~ 50 mtorr throughout the synthesis with a flow rate of about 0.61/min. The laser source was the fourth harmonic of a pulsed Nd-YAG laser, with a wavelength of 266 nm, and a pulse width of 10 ns, repetition rate of 10 Hz, and pulse energy of typically 40 mJ/pulse. The laser beam was focused down to ~ 0.5 mm diameter spot on the In target causing the ablation. The ablated products were collected downstream with a microporous cellulose nitrate membrane filter. The resulting InN powder was characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS). Optical properties were studied using photoluminescence spectroscopy (PL).

4:00 PM 12.7
OPTICAL AND STRUCTURAL CHARACTERISTICS OF GOLD NANO CRYSTALLITES EMBEDDED IN A DIELECTRIC MATRIX. A.K. Sharma, A. Kirt, J. Narayan, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; J.F. Muth, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC.

Nanocrystalline materials are receiving enormous attention of the scientific community due to their novel physical and chemical properties. In this context, studies of metal nanocrystallites embedded in a dielectric matrix are of fundamental importance from the point of view of tailoring optical properties of the composite. However, their fabrication with the control on size variation is an experimental challenge. The techniques such as ion implantation of metallic clusters in the host dielectric matrix and subsequent annealing have been employed for such studies. However, PLD has an edge over other
techniques to precisely control the sizes of these particles and placing them in a desired location in the host lattice. By changing the thickness of the magnetic film, the collective excitation frequency or surface plasmon frequency of the metal can be varied, and thus, the optical absorption frequency can be altered. We have fabricated a novel multilayer structure comprising alternate layers of gold nanoparticles and gold phthalocyanine dye on glass substrates. The results point out one of the success of PLD in tailoring the optical and mechanical properties of these composites with thickness and size.

4:15 PM 12:8
SYNTHESIS AND CHARACTERIZATION OF SELF-ASSEMBLED NANOSCALED IRON PARTICLES PRODUCED IN A FLOW REACTOR BY LASER PYROLYSIS. H. Hoffmeister, MPI fuer Mikrostrukturphysik, Halle, GERMANY; F. Huisken, B. Koh, MPI fuer Stroemungsforshung, Goettingen, GERMANY; R. Alexandrescu, S. Ceojculescu, A. Crumteanu, I. Morjan, I. Voicu, National Institute for Lasers, Plasma and Radiation Physics, Bucharest, ROMANIA; L. Diamandescu, National Institute for Materials Physics, Bucharest, ROMANIA.

Iron and iron composites present a particular interest due to their magnetic and catalytic properties which could be highly enhanced if particle in the nanometric size range were used. Nanoscaled iron particles, self-assembled in filaments have been prepared via laser pyrolysis of 2-pentanone in a flow reactor. Using the sensitizer C8H4, a CW CO2 laser with power of 70 Watt was employed. The samples have been carefully prepared before exposing them to air. Selected area electron diffraction (SAED) studies revealed the presence of α-Fe, with important contributions from magnetite (Fe3O4) and hematite (α-Fe2O3). Results of Moessbauer spectroscopic analysis were in rather good agreement with these findings. The studies were complemented by high-resolution electron microscopy (HREM) yielding information on further details such as local structures, interfaces and particle size distribution. The amorphous carbonaceous component of particles was estimated by thermal extraction and IR transmission spectroscopy. A comparison with previous reported results on iron carbide-based nanocomposites, synthesized at higher laser power (~180 Watt) is also presented.

4:30 PM 12:9
NOVEL ZINC NANOCRYSTALLINE COMPOSITES BY PULSED LASER DEPOSITION. Ravi K. Venkatesan, A.K. Sharm, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have developed a novel processing technique to fabricate free zinc nanocomposites. In this method, pulsed laser deposition of zinc in conjunction with a few monolayers of W is used to control the grain size of the composite. The grain size was controlled by the thickness of zinc and the substrate temperature. The role of W is to ensure the nucleation of zinc islands, and it is also insulating in zinc. Using this approach, we have fabricated nanocomposite powders ranging from 10 nm to 100 nm. The nanocomposite powders were synthesized at higher laser power (~180 Watt) and also presented.

SESSION 3: POSTER SESSION: LASER-SOLID INTERACTIONS FOR MATERIALS PROCESSING

Chairs: David P. Norton, Dhananjay Kumar, Clinton B. Lee, Kenji Ebihara and Xiaoming Xi
Tuesday Evening, April 25, 2000
8:00 PM
Salon 1-7 (Merritt)

33.1 PLASMA AND DLC FILM CHARACTERISTICS FROM PULSED LASER ABLATION OF SINGLE CRYSTAL GRAPHITE AND AMORPHOUS CARBON: A COMPARATIVE STUDY EMPLYING ELECTROSTATIC PROBE MEASUREMENTS. R.M. Mayo, J.W. Newman, Department of Nuclear Engineering, North Carolina State University, Raleigh, NC; Y. Yamagata, Department of Electrical and Computer Engineering, Kumamoto University, Kumamoto, JAPAN; A. Sharma, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

In a continuing investigation of plasma plume features yielding high quality DLC films, we have applied plasma plume diagnosis and film characterization to examine differences with KrF laser ablation of both amorphous carbon (a-C) and single crystal graphite (SCG) targets. The advancing plasma plume produced by these structurally different targets are observed to possess quantitatively similar total heavy particle inventory, ionized fraction, and electron thermal content, yet quite different kinetic energy, electron probe, C2 formation mechanism, and complex molecule formation. Plasma electron density is found to be ~1.5x10^12 lower near the target in SCG than a-C plumes consistent with mass loss inventory measurements, whereas the other plume properties are estimated in the range ~15-15% for both target cases. Plasma electron temperatures are observed to reside in the range 1-3 eV, with those in SCG plumes ~10-30% greater than a-C at all spatial positions downstream of the targets. For both target cases, the kinetic energy content from the target for which radiation is the most likely loss mechanism for these non-interacting plumes propagating in vacuum. All observations support the conclusion that the SCG target plume is populated with heavier, more complex molecules (perhaps fullerenes and nanotubes) than those in a-C. The latter have been shown to be predominantly comprised of C and C^+ under vacuum conditions with the formation of C2 at high fill pressures [R. M. Mayo, et al., J. Appl. Phys. 86, 2865 (1999)]. A significantly smaller profile penning factor for SCG plumes suggests this conclusion. Less energetic and slightly lower temperature SCG plume conditions are consistent with reduced penning and more massive plasma species. Plasma plumes from SCG targets exhibit laser energy (E_l) dependent penning, again consistent with more complex molecules increasingly dissociated with E_l increase. The E_l dependence further suggests the potential for control of particle size distribution and probe electron probing, therefore ion production. The observation of harder films produced from SCG targets at lower E_l is also consistent with this fracture scenario. Further supporting the case for more complex structures with greater hardness are the micro-Raman results indicating strongly heterogeneous films deposited by SCG target ablation even under vacuum conditions. Energy balance estimates indicate that ion kinetic energy dominates the balance and that SCG ablation releases about twice the number of 12C atoms from the target per unit E_l. In addition, high pressure background fill indicates lesser plasma energy attenuation for SCG plumes, again suggesting the presence of massive particles.

33.2 IMPROVEMENT OF CAVITATION EROSION RESISTANCE AND CORROSION RESISTANCE OF BRASS BY LASER SURFACE MODIFICATION. K.P. Tang, F.T. Cheng, The Hong Kong Polytechnic Univ, Dept of Applied Physics, Hong Kong, P.R. CHINA; H.C. Miu, The Hong Kong Polytechnic Univ, Dept of Manufacturing Engineering, Hong Kong, P.R. CHINA.

Laser surface modification of brass (Cu-38Zn-1.5Pb) using AISiFe and NiCrSiB alloy was achieved by using a 25W continuous wave Nd:YAG laser with the aim of improving the cavitation erosion resistance and corrosion resistance. The SiC powder was deposited on brass substrate by thermal spraying to a thickness of 1.54-3.00μm, followed by laser beam scanning to effect melting, mixing and alloying. A modified surface was achieved by overlapping of adjacent tracks. The cavitation erosion resistance and the microhardness characteristics of the laser surface modified specimens in 3.55% NaCl solution at 23°C were studied by means of a 20K Hz ultrasonic vibrator at a peak to peak amplitude of 30 μm and a potential of 10 V respectively. The cavitation erosion resistance of the specimens modified with AISiFe and NiCrSiB was improved by a factor of 3 and 6 respectively, compared with that of the brass substrate. Potentiodynamic test, however, indicated that the corrosion resistance of specimens modified with AISiFe deteriorated, as evidenced by a shift of the polarization curve towards higher current densities. On the other hand, the corrosion resistance of specimens modified with NiCrSiB was significantly improved, as evidenced by the presence of a passive region (from 175 mV to 120 mV) and a reduction in the anodic current density by at least an order of magnitude compared with the substrate at the same anodic potential. The hardness profile and the compositional profile were measured using a Vickers hardness tester and EDX respectively. The morphological and spectral characteristics of the specimens were investigated with the aid of SEM and optical microscopy.
The F_2 laser is a promising source for direct etching of microstructures and the precise shaping of optical-grade surfaces on wide bandwidth materials such as fused silica [1]. The threshold fluence for material removal is high in glass (>1 J/cm²), and radiation exposure to the underlying bulk glass can therefore reach moderately high laser doses (>10^7 J/cm²) with only several micromachining laser pulses. Because of the high photon energy, 7.9 eV, radiation damage in the form of material compaction, refractive-index change, and material stress can develop. Stress-induced distortion of the surface relief and alteration of the material refractive index is an important limitation that degrades the optical performance of the sample and limits the precision with which micro-optical components can be laser micromachined.

We report here our experimental results and stress analysis of fused silica (Corning 7940) samples ablated with 157-nm laser radiation. Plastic strain of laser-ablated samples (160 micron thick) was monitored with an optical interferometer microscope. The bending plate method provided a measure of the stress and showed that residual stresses on the sample were tensile at the ablated surface. By thinning the sample with chemical etching, the thickness and profile of the laser-ablated stresses were obtained. These ablation results are contrasted with low-fluence results where refractive-index changes were induced without material ablation. XPS analysis revealed that surfaces undergo a stoichiometric change (the loss of silicon) only when surfaces were ablated. Little change was noted when exposures at sub-ablation fluence were applied. Possible mechanisms for these changes and their relation to material stresses will be discussed.


J3.4 LASER INDUCED FLUORESCENCE MEASUREMENT OF PLASMA PLUME (PLMG) USING PULSED LASER DEPOSITION OF DIAMOND-LIKE CARBON. Yukiko Yamanaka, Yuji Kozmi, Pumiki Mitsuji, Tomoki Inoue, Kenji Ishihara, Kummoto Univ, Dept of Electrical and Computer Engineering, Kumamoto, JAPAN; Ajay Sharma, Jugdhit Nijjar, North Carolina State Univ, Dept of Materials Science and Engineering, Raleigh, NC; Robert M. Mayo, North Carolina State Univ, Dept of Nuclear Engineering, Raleigh, NC.

Pulsed laser deposition (PLD) has been employed to fabricate superior quality diamond-like carbon (DLC) films with sp³ formation exceeding 80%. However, the detailed mechanism of the PLD process to prepare the DLC film has yet been understood. In order to prepare high quality DLC film and to improve the potential of the PLD, it is desirable to diagnose and establish correlation between plasma composition and properties of DLC films. Laser induced fluorescence (LIF) spectroscopy is a powerful tool to diagnose such dynamic phenomena, and is useful to establish correlation between plasma composition and film properties. In this paper, we describe quantitative study using LIF spectroscopy on ablation plasma during KrF excimer PLD of DLC film. A KrF excimer laser was used to ablate diamond-like carbon (DLC) and a 45 degree angle of 45 degrees. A dye laser (Lambdam Fluorescein, 560 nm) was tuned at 516.50 nm to excite C2 molecules, and introduced into the ablation plume along with the target surface. The probe laser was turned off at half the intensity of the ablation laser after the KrF laser irradiation. Laser induced fluorescence of 563.49 nm (001) D²⁺ 4fD⁻ was successfully detected at right angle of both beams by a monochromator equipped with a photomultiplier. LIF detection on a target surface was carried out at 1 mm from the target surface in high vacuum. The LIF intensity increases with increase of the probing laser delay until 200 ns, and decreases with the further delay. The LIF was observed about 1.2 μs after the ablation laser irradiation, while optical emission from the ablation plume was observed about 200 μs. It suggests that C2 molecules are formed near the target as a result of recombinative formation of carbon atoms and/or dissociation of heavier particles.

J3.5 STRUCTURAL CHARACTERIZATION OF LASER LIFT-OFF GaN. E.A. Schel and M. Kelch, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; W.S. Wong, N. Chung and T. Sinda, Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA.

Laser lift-off and bonding offers a promising route for the integration of dissimilar materials in electronic and optoelectronic applications. In our work, a KrF pulsed excimer laser is used to selectively decompose the interface between high vapor pressure epitaxy (HVPE) grown GaN and its free-standing substrate. This yields a layer of single crystal GaN. [Wong, et al. APL 1998]. Herein, we use transmission electron microscopy (TEM) to characterize the effects of the lift-off process on the structural and chemical properties of the resulting layer. High-resolution transmission electron microscopy (HRTEM) and contrast microscopy indicate that the interface between the HVPE GaN and the sapphire substrate before lift-off is highly strained and defective [as was anticipated from the 14.2% lattice mismatch between these two materials]. This indicates that there are regions of amorphous material spaced approximately 50 nm apart along the interface. Additionally, a high density of stacking faults is observed. Microscopy of the GaN and Al₂O₃ layers following lift-off shows that the laser determines the layer directly at the interface between the two materials, and that the GaN layer remains a single crystal. A substantially lower density of stacking faults is observed in the epilayer, indicating that the thermal energy deposited by the optical flux actually decreases the structural perfection of the GaN. Scanning transmission electron microscopy and energy dispersive x-ray spectroscopy show slight interdiffusion of aluminum into the GaN and Ga into the sapphire, but only within 20 to 30 nm from the resulting interface. These results indicate that the laser lift-off process can yield perfect materials, well suited for device integration.

J3.6 DIAMOND-LIKE CARBON FILM GROWTH FOR HIGHLY IONIZED DUAL-LASER GENERATED PLASMAS. Alfred M. Miyawa, Sarah Watanabe and Priyab Mukherjee, Laboratory for Advanced Materials Science and Technology (LAMSAT), Department of Physics, University of South Florida, Tampa, FL.

One of the main advantages of the dual-laser ablation process for the growth of high-quality thin films is the ability to control the degree of ionization in the material plasma. Ionization yields in excess of 60%, in comparison with 4-10% in single laser ablation, are possible with dual-laser ablation. The spatially overlapping and temporally synchronized excimer and CO₂ laser pulse combination creates plasma temperatures in excess of 25,000K at the target which leads to the enhanced ionization. It is well known that in the growth of diamond-like carbon (DLC) films the incidence of highly energetic carbon ions on the substrate aids the formation of covalently bonded carbon growth which is responsible for diamond-like behavior. In this paper, the advantages of dual-laser ablation for DLC film growth are presented. We have used ion probe measurements and emission spectrometry techniques to study the enhancement in ionization and spatial ion distribution in dual-laser ablated diamond films. Films deposited on Si substrates by single and dual-laser ablation at different substrate bias conditions have been analyzed using Raman spectroscopy. The broad Raman spectra produced by these amorphous films have been deconvoluted to yield two peaks, one characterizing the sp² bonding (D-band) around 1350 cm⁻¹ and the other representing the sp³ (G-band) around 1550 cm⁻¹. The ratio of intensities corresponding to these peaks have been used to gauge the relative sp³ content of the deposited films and clearly demonstrate the advantage of using dual-laser ablation for DLC growth. This work is supported in part by the National Science Foundation (Grant No. DMR-962114) and the US Department of Energy (Grant No. DEF-05-98ER12190).

J3.7 OPTICAL PROPERTIES OF TANTALUM OXIDE FILMS DEPOSITED ON BK7 BY LASER ABRAZION. S. Boughaba and M. Islam, National Research Council Canada, Integrated Manufacturing Technologies Institute, London, Ontario, CANADA.

Thin amorphous films of tantalum oxide (TaOx) films were grown on borosilicate glass (BK7) substrates by KrF (248 nm) excimer pulsed laser ablation of a Ta₂O₅ target, in an oxygen environment. The substrates were heated to a temperature of between 350°C and 400°C, while the oxygen pressure was set in the range 5 to 30 mTorr. The films were found to be stoichiometric Ta₂O₅ for O₂ pressures above 10 mTorr. The refractive index and extinction coefficient of the TaOx films were simultaneously measured by both spectrophotometry and transmittance, with wavelengths in the range 250 to 850 nm and 420 to 1000 nm, respectively. For all growth conditions, best fitting to the reflectance and transmission curves was achieved by assuming two layer optical model of the BK7 substrate. As 0.1 nm thicknesses decreases between 2 and 2.5, both layers was obtained for both layers, along with extinction coefficients of 10⁻⁷ to less than 10⁻⁴, depending on the processing parameters. High-resolution cross-sectional electron microscopy was used to investigate the vicinity of the TaOx/BK7 interface.

J3.8 INVESTIGATION ON LASER-INDUCED EFFECTS IN NANOSTRUCTURE FABRICATION WITH ULTRASHORT SCANNING TUNNELING MICROSCOPE TIPS IN AIR AMBIENT. Z.H. Mi, Y.F. Lu, W.D. Song and W.K. Chiu, Laser Microprocessing Laboratory, Department of Electronic Engineering and Dan Storge Institute, National University of Singapore, Singapore, SINGAPORE.

Nanofabrication using lasers in combination with a scanning microscope (STM) has been reported in the past several years. Dual-laser mechanisms have been proposed for these structures. Some researchers suggested that the underlying mechanism
be based on the optical enhancement of the tip, while others proposed that the thermal expansion of the tip is the primary reason. Due to great controversy over the mechanism of enhancement, a detail investigation is necessary. In this paper, we report our investigation on the kinetics of nanostructure fabrication on gold films on H-passivated Ge surfaces. The relationship between the current and the tip-sample distance of the STM junction was measured for both gold films and H-passivated Ge surfaces. The tip-sample distance for gold films under a electrochemically etched W tip is approximately 2 nm, while that for H-passivated Ge surfaces is much higher. The thermal expansion of the tip due to laser irradiation was calculated. From the comparison of the thermal expansion length and the tip-sample distance, we can reach the conclusion that for gold films, thermal mechanical indentation is the primary reason of the non-adhesion, while for H-passivated Ge surfaces, optical enhancement is the only reason.

### 13.9 MAGNETIC FIELD GENERATION AT EARLY STAGE OF KFe EXCIMER LASER ABLATION OF SOLID SUBSTRATES

M.H. Hong, Y.F. Lu and A. Bong, Laser Microprocessing Laboratory, Dept. of Electrical Engineering and Data Storage Institute, National Univ. of Singapore, SINGAPORE.

Magnetic field generation at early stage of KFe excimer laser ablation of solid substrate (delay time less than 200 ns) is investigated. Based on classical electrodynamics, fast emission of electron and positive ion at the beginning of laser ablation emits out an electromagnetic field nearby. A tiny iron probe wrapped with 50 µm coil is applied to detect the magnetic field at the dynamic magnetic field. It is found that the signal waveforms are closely related to probe distance from the laser spot. For probe distance less than 1 mm, the signal shows a double peak distribution with the negative peak appearing first. The peak duration is less than 30 ns. As the probe distance increases, the positive peak amplitude reduces much faster that the negative peak. The positive peak disappears for probe distance up to 1 mm and the signal waveform becomes a negative peak with its duration around 50 ns. Mechanism of the space- and time-resolved distribution of the dynamic magnetic field at the early stage of laser ablation is analyzed. Dependence of the magnetic field signal on laser fluence, substrate bias and pulse number is also studied during laser ablation of solid substrate and removal of organic contamination on the substrate surface.

### 13.10 INFLUENCE OF SUBSTRATE TEMPERATURE ON BARIUM FERRITE FILMS PREPARED BY LASER DEPOSITION

W.D. Song, Y.F. Lu, W.J. Wang, T.C. Chong, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, Singapore, SINGAPORE.

Barium ferrite has been identified as one of the candidates for high-density magnetic recording. Till now, barium ferrite films have been prepared by a few groups using sputtering and laser deposition. In this article, we report some recent findings on the properties of barium ferrite films prepared by laser deposition with post annealing, in-situ heating and varying substrate temperature during film growth. The films with in-situ heating exhibits a preferential c-axis orientation normal to the film plane and large perpendicular magnetic anisotropy. The grains in the film have good crystallinity with hexagonal symmetry. The perpendicular and in-plane coercivities are 28 and 1.4 kOe, respectively. While the film with a post annealing exhibits both c-axis orientation normal to the film plane and in-plane c-axis orientation and has almost isotropic properties. The grains in the film show both circular and elongated shapes. The perpendicular coercivity and in-plane coercive are 5.1 kOe. For the film deposited with a varying substrate temperature, the perpendicular and in-plane coercivities reach 5.7 and 5.5 kOe respectively. The results show that magnetic properties, grain shape and crystalline orientation of the film deposited with a varying substrate temperature are close to the film deposited with a post annealing and different from the film deposited with in-situ heating.

### 13.11 STUDY OF TETRAHEDRAL AMORPHOUS CARBON WITH DIAMOND INCLUSIONS SYNTHESIZED BY HYPERTHERMAL CARBON SPECS 3.38. J.P. Zhou and Z.Y. Chai, National Industrial Research Institute, Tashkent, JAPAN and 3ION Beam Laboratory, Shangai Institute of Metalurgy, Chinese Academy of Sciences, Shanghai, CHINA; T. Yano, T. Oide and M. Yonedo, Shikoku National Industrial Research Institute, Tashkent, JAPAN.

Tetrahedral amorphous carbon (t-C) films have been synthesized by two hyperthermal processes: pulsed laser ablation (PLA) and filtered arc deposition. The case of PLA and filtered arc deposition will be remarkably effect on the structure and properties of t-C. Particle density and size reduced with decreasing fluence; however, film density and optical properties were optimized at moderate fluence. The maximum density (~3.0 g/cm³) and sp² content (~80%) were achieved at 840 mJ cm⁻² fluence for PLA. Transmittance, optical band gap, and UV absorption edge were also reach to extreme values at this fluence. By calculating film thickness from interference of reflection spectrum, we found that the minimum interval between calculated and measured thickness decreases by half, and the optical band gap decreased towards that of amorphous carbon (a-C), which could be attributed to the increase of the fraction of sp² hybridization and the formation of nanocrystalline or hexagonal diamond inclusions according to phonon density of states (DOS) calculation. Moreover, benzene-like structure was also observed in PLA deposited films. On the other hand, more tetrahedrally bonded films (~85% sp² content) prepared by FAD were evaluated by HRTEM, EELS, UV-Visible-NIR, SE, and IR spectroscopy, double-crystal XRD and nano-indentation. An energy window for optimizing t-C quality was found to be similar to the fluence window of PLA case. Structural and physical properties were compared between films synthesized by these two processes. The more precise control of hyperthermal carbon species and energy in FAD is favorable to achieve high quality t-C.

### 13.12 PULSED ELECTRON BEAM ABLATION OF Ga₅Se₃.

I.A. Serebryakov with A. Tikhomirov and Serhei Malkov, Cit of Optoelectronics, Inst of Applied Physics, Academy of Sciences of Moldova, Kishinev, MOLDOVA.

Pulsed electron beam ablation has been applied for preparation of high-quality Ga₅Se₃ (cis) thin films. This method is concerned to be analogous to pulsed UV-laser ablation but its capital costs are many times lower. Comparison of electron beam ablation versus laser ablation by plasma plane diagnostic studies has been performed in [1] where it is established that there is a relative amount of neutral species for the former one. In this paper we compare the properties of the CIS films deposited by pulsed electron beam ablation with the films deposited by pulsed laser ablation. In the case of pulse laser ablation, the CIS deposition was implemented by a pulsed plasma induced high current and magnetically self-pumped electron beam produced in a low pressure system with an electron energy of 600 eV, which has been observed for the CIS films deposited by pulsed laser ablation. Moreover, the results of the deposition of the low substrate temperature CIS films by means of the pulsed electron beam under different beam parameters are presented.


### 13.13 EPITAXIAL ZnO FILMS GROWN BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION (UV-PLD) Y. Gao, V. Corcione, A. Singh, Department of Materials Science & Engineering, University of Florida, Gainesville, FL; J. Perriere, Groupe de Physique des Solides, Universites Paris VII et VI, Paris, FRANCE; D. Oruchin, Laser Department, National Institute for Laser, Plasma, and Radiation Physics, Bucharest, ROMANIA.

ZnO is an interesting semiconductor material that has been used for transparent conductive and piezoelectric applications. It also exhibits nonlinear optical and piezoelectric properties and has been used as a light modulator, a phase optical waveguide, or for surface acoustic wave devices. Some of these applications require the growth of epitaxial, high quality ZnO layers on sapphire or other single crystal substrates. Pulsed laser deposition (PLD) of ZnO has been one of the most used methods to grow high quality films at relatively moderate temperatures. However, the PLD growth of high quality epitaxial ZnO films requires substrate temperatures around 1000 K, which are too high for many applications. We have developed an in-situ ultraviolet-assisted PLD (UV-PLD) technique where an ultraviolet source was added to the deposition chamber. The UV source irradiates the laser plasma plume with high energy photons that increase the surface mobility of the adatoms and photodissociate the molecular oxygen employed during reactive deposition. By using the UVPLD technique, we were able to obtain low-resistivity ZnO films by pulsed laser deposition using electron microscopy, and x-ray diffraction investigations, high quality
epitaxial ZnO films on sapphire at a substrate temperature of only 775 K, more than 200 K lower than that usually employed during conventional techniques. This is due to the process and characteristics of these UVPD grown ZnO films will be presented. These results clearly illustrate the advantages of this technique for the growth of high quality ZnO thin films at moderate temperatures.


Although colossal magnetoresistance in lanthanum magnesium oxide (LCMO) thin films is known since a long time, the effect of oxygen content and crystallinity on the properties of LCMO films has not been clearly understood. It is in this context that we have performed a systematic study to resolve the effects of these two parameters on properties of LCMO films by subjecting them to different post-deposition heating treatments. A series of LCMO thin films have been grown in situ on [100] LaAlO₃ substrates using a pulsed laser deposition technique under identical conditions. These films were subjected to the following post-deposition heating treatments, 500°C oxygen anneal for 12 hours, 900°C Ar anneal for 2 hours, 900°C Ar oxygen anneal for 2 hours, 900°C Ar oxygen anneal and quenched to room temperature and 500°C vacuum annealing for 1 hour. As deposited LCMO films were found to be a transition metal and an MR ratio (defined as [R(0)-R(H)]/R(0)], where R(0) and R(H) are the resistance in zero and applied magnetic fields] of 100% [2]. The samples subjected to 500°C oxygen, Ar and vacuum annealing have shown deterioration of magnetoresistance properties. The films subjected to 900°C annealing in Ar and oxygen ambient have shown a significant improvement in the metal-insulator transition temperature [240 K]. The oxygen content and crystallinity of the films, before and after the post-deposition treatments, were measured using Rutherford Backscattering Spectroscopy (RBS) and x-ray diffraction (XRD) measurements. Based on our experimental results, we will present an in-depth discussion to deconvolute the effect of oxygen content and crystallinity in the determination of magnetoresistance properties of lanthanum magnesium oxide thin films.

13.15 EPITAXIAL GROWTH OF β-C₃N₄ ON A NITRIDED DIAMOND SURFACE BY NITROGEN-ARC-DISCHARGE-ASSISTED LAYER ABLATION DEPOSITION. Pei-Nan Wang, Ning Xu, Xia-Yong Ying, Zhi-Feng Ying, Zheng-Ping Liu and Wei-Dong Yang, Ruzhan University, State Key Joint Lab for Materials Modification by Triple Beams, Dept of Physics, Shanghai, CHINA.

A diamond film was nitrided by low-energy nitrogen ion implantation. The nitrided ion source was a homemade device using glow discharge to generate nitrogen ion beams. The mass spectrum shows that the ratio of N⁺/N₂⁺ is as high as 5/1. The Raman spectrum shows that the β-C₃N₄ phase was formed in the diamond surface after nitrogen implantation. Epitaxial growth of β-C₃N₄ was carried out on this nitrided diamond film by nitrogen-arc discharge-assisted laser ablation deposition. A high-purity graphite rod was ablared by a frequency doubled Nd:YAG laser. A pure nitrogen gas flow was passed through a magnetically cooled and arc-shaped source to generate a reactive nitrogen atom beam. The temperature of the substrate was kept at 600 degrees during deposition. The X-ray photoelectron spectrum of the produced film shows the existence of the nitrogen content. The structure of the film was characterized by Raman and infrared (IR) spectrometry. There were eight narrow Raman peaks observed in the range of 156-1950 cm⁻¹. Seven of them match well with the calculated Raman frequencies of the C₃N₄ molecule containing the β-C₃N₄ phase. No such Raman peaks were detected in this region when carbon nitride films were synthesized on silicon substrates using the same method. The IR expansion spectrum of the film shows two peaks at 1444 and 1290 cm⁻¹, which also match with the calculated ones of β-C₃N₄.

13.16 FUNCTIONALLY GRADIENT DIAMONDLIKE FILMS. R.J. Necoray, Wake Forest University, School of Medicine, Winston-Salem, NC, Q. Wei, A.R. Sharma, J. Necoray, North Carolina State University, NSF Center and Dept of Materials Science & Engr, Raleigh, NC.

We have fabricated diamondlike carbon protective coatings on Ti-6Al-4V and Co-Cr alloys which are used for hip prostheses. Using optimized laser parameters, we are able to produce DLC films at room temperature. These films eliminate oxidation, wear and the chemical nature of the film and have revealed details of the microstructure such as be reduced by doping with Ag and Cu in small concentrations and improve adhesion and wear of these films. In addition, the Ag-doped DLC films also exhibit outstanding electrical properties. The dependence of the UVPLD grown ZnO films will be presented. These results clearly illustrate the advantages of this technique for the growth of high quality ZnO thin films at moderate temperatures.


LiMn₂O₄ films were grown onto Si substrates heated at temperature lower than 300°C using a pulsed laser deposition (PLD) from a sintered composite target (LiMn₂O₄+Li₂O) irradiated with a Nd:YAG laser. The structural characteristics of these films have been carried out by Raman scattering, [R] spectroscopy which probe the local environment of Li, Mn, O, and N in the LiMn₂O₄ films. The spectra of PLD LiMn₂O₄ films have been investigated in a function of various growth conditions, i.e., substrate temperature, partial oxygen pressure in the deposition chamber, and target composition. X-ray diffraction data and RS measurements show that such a film crystallized in the spinel structure (P63m space group). Information for the structural quality of the PLD LiMn₂O₄ films can be given considering the Raman data using the shape and the frequency of two groups of peaks located in the low- and high-frequency region of the spectra. The effect of target composition is clearly observed. When the PLD films are grown from target with Li₂O/(Li₂O+Mn₂O₃) less than 0.7 and the stretching Mn-O peak is broadened toward the high wavenumber side due to the high distortion of MnO₆ octahedra. These spectroscopic results indicate that the concentration of target composition, substrate temperature (T=300°C), and partial oxygen pressure (P=0.00 Torr) promote reconstruction of the stoichiometric LiMn₂O₄ spinel framework.

13.18 SURFACE MORPHOLOGY OF PZT THIN FILMS PREPARED BY PULSED LASER DEPOSITION. Msanuki Yamamoto, Masanitru Nagumo, Saga Univ., Dept. of Chemistry and Applied Chemistry, Saga, Japan; Kenji Ebihara, Kamaomoto Univ., Dept of Electrical and Computer Engineering, Kamaomoto, Japan.

Pulsed laser deposition (PLD) has been used successfully in synthesizing many kinds of films, because PLD is a very attractive method, especially for oxide film preparation which guarantees the congruent transfer of highly nonthermal eroded target material to the growing film. High initial laser energy rate of heating and energetic plasma beam results in high kinetic and internal excitation energies of ablated species to mass growth film and to promote surface solid state reactions. In this paper, PbZr₀.₅₂Ti₀.₄₈O₃ (PZT) thin films have been grown on MgO substrate using a pulsed KrF excimer laser deposition system. The films were deposited under the following oxygen pressure range 0.1-0.2 Torr at substrate temperature of 550°C and laser fluence of 2.2 J/cm². The ambient gas pressure dependence of surface morphology was investigated using the scanning probe microscopy. The size of PZT particles was strongly dependent on the ambient gas pressure. At a 100 mTorr oxygen pressure, the diameter of PZT particles was about 30 nm, and then increasing an oxygen pressure increases the particle size. Experimental data for the ambient gas pressure dependence of the size of PZT particles are found to fit well to a power law dependence of PZT particles size, which indicate diameter of PZT particle and oxygen gas pressure, respectively.


We have synthesized epitaxial cubic Zn,Mg₁₋ₓO thin films with x up to 0.2 on MgO (100) substrates using pulsed laser deposition. In this composition range, Zn,MgO phase is cubic with lattice constant of the film (a=4.21 Å) matching closely with that of the substrate (a=4.21 Å). This system provides an opportunity to integrate ZnMgO films with silicon substrate (a=5.43 Å) via domain matching epitaxy where 4 lattice units of the film match with 3 of the substrate. We have successfully fabricated 3D epitaxial heterostructures of ZnMgO/TiN/Si [100] layers. The characterization of layers was accomplished by X-ray diffraction, high resolution transmission electron microscopy (HRTEM), Rutherford backscattering spectroscopy ion channeling (RBS), and optical measurements. HRTEM results have been obtained on single crystal nature of the films and have revealed details of the microstructure such as...
defects. The ion channeling yield as low as 3% was achieved in the epitaxial films indicating a good quality of the crystal. Optical results have also been obtained in this work. These single-crystal films with cubic symmetry have a potential for a number of applications in microelectronic devices.

**J3.20**

**IRON AND IRON CARBIDE THIN FILMS AND NANO-ARCHITECTURES OBTAINED BY LASER-ASSISTED CVD**

**METHODS:** R. Acosta, J. Garcia Carpio, J. Varela, M. A. Garcia, E. Gómez, J. Marín, J. Casado, and M. J. Pardo, Instituto de Física de Microelectronica, Universidad de la Sabana, Tunja, Colombia. **Abstract:** The laser-assisted chemical vapor deposition (LACVD) technique is a promising method for the deposition of thin films and nano-architectures. This technique involves the use of a laser to heat a solid substrate to a high temperature, allowing the atomic vapor deposition process to occur. The use of laser energy can lead to a more controlled deposition process, allowing for the fabrication of high-quality films with specific properties.

**J3.21**

**LOW TEMPERATURE GROWTH OF BARIUM STRONTIUM TITANATE FILMS BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION.**

**DEPOTORO, V. CRACK, D. R. HOWARD, A. SVIRSKAV, N. DOSS, AND R. K. SINGH,** Department of Materials Science and Engineering, Florida State University, Tallahassee, FL, USA. **Abstract:** The growth of crystalline barium strontium titanate (BST) thin films is of great importance for the development of new electronic and photonic devices. In this study, we investigate the growth of BST films using a pulsed laser deposition (PLD) technique at low temperatures. The films were deposited on silicon substrates and characterized using X-ray diffraction (XRD) and Raman spectroscopy. The results show that the films exhibit a cubic perovskite structure with high crystallinity and good film quality.

**J3.22**

**TANTALUM NITRIDE THIN FILMS SYNTHESIZED BY PULSED Nd:YAG LASER DEPOSITION METHOD.**

**H. KAWASAKI, K. DOI, S. HIRAI, AND Y. SADOMI,** Department of Electrical Engineering, Nagaoka University of Technology, Nagaoka, Japan. **Abstract:** Tantalum nitride (TaN) films have been deposited on silicon (100) substrates using a pulsed Nd:YAG laser deposition method. The films were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the films have a cubic fluorite structure and exhibit good adhesion to the silicon substrate.

**J3.23**

**INTRODUCTION TO THE MAGNETORESISTIVE LNO0.8Sr0.2MnO3 (LSMO) FILM AND FERROELECTRIC PbZr0.5Ti0.5O3 (PZT)**

**STRUCTURE AND PROPERTIES OF THE MAGNETORESISTIVE LNO0.8Sr0.2MnO3 (LSMO) FILM AND FERROELECTRIC PbZr0.5Ti0.5O3 (PZT)**

**SESSION J4/V5: JOINT SESSION: LASER DIRECT WRITING**

**Chair:** Herbert Herrmann, **Wednesday Morning, April 26, 2000**

**NOTE EARLY START**

**8:15 AM J4.1/V5.1**

**AN IMPROVED METHOD OF UV LASER DIRECT-WRITE DEPOSITION OF MATERIALS FOR MICROELECTRONICS**

**APPLICATIONS:** A. M. Bakr, D. N. Matters, and M. T. Dunning, Potomac Photonics, Inc., Irwin, MD. **Abstract:** We demonstrate a new laser direct-write method, a process that transfers materials directly from a ribbon to a substrate, thereby enabling feature widths as small as 100 nm. This process offers the promise of fabricating interconnects and passive electronic components at high speed, however, there are practical challenges that must be addressed for promoting the process from research scale to production. The main advantages of 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 pick-and-place system with adjustments for ribbon and substrate manipulations. Conducting lines deposited from Ag ink on semi-conductive substrates by this method under the proper 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, processing conditions and other factors pertaining UV laser parameters.

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

**LASER-GUIDED DIRECT WRITING OF ELECTRONIC COMPONENTS.**

*Michael J. Bennis, Marcelino Basa, Bruce H. King and W. Doyle Miller,* Optomec Design Company, Albuquerque, NM. **Abstract:** 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 temperatures (<100°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 novel 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 ± 1 micron feature sizes and resistance values of ≈10 Ω. Likewise, single phase, barium titanate has been densified at low processing temperature. Deposition has been demonstrated on a wide range of substrates including aluminum, glass, polycrystalline, barium titanate, PVC plastic, and various metals.

9:00 AM J4.3/V5.3**

**LASER INDUCED ETCHING OF Si WITH N3 USING CuBr LASER.**

*E. Horns,** M. P. Marschke,** L. Zamboni,** Dept. of Condensed Matter Physics, Stockholm, Sweden. **Abstract:** The magnetoresistive LNO0.8Sr0.2MnO3 (LSMO) film and ferroelectric PbZr0.5Ti0.5O3 (PZT) heterostructures were prepared on the MgO (100) single crystal substrates by RF sputter pulsed laser deposition (PLD) technique. The LSMO film deposited at 850°C, O2 (1%)/Ar and laser energy density of 21 J/cm² (30 Hz) has a resistivity peak temperature of 295K. The X-ray diffraction pattern showed (001) axis orientation. The Atomic Force Microscope image showed very smooth surface morphology (maximum roughness < 1 nm) with the mean grain size of about 100 nm. The highly c-axis oriented ferroelectric PZT film was prepared on the LSMO/MgO, and the FWHM of rocking curve about PZT (002) was 0.82°. The polarization-electric field characteristics of the As/PZT/LSMO/MgO capacitor, indicated remnant polarization of 22 μC/cm² and coercive field of 5kV/cm (applied voltage 10V, 1kHz).
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 528 nm. The laser beam was focused to 100 μm in the range of 10.4 W with repetition rate - 20 kHz and the pulse duration - 60 ns. NF3 was used as partial pressure in the range of 1 - 1000 mbar. The basic process parameters were varied in the range scanning speed from 0.5 to 10 μm/s (AFM) and 500 μm/s to 400 μm/s, 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 sample on the etched depth were studied. The etched depth was in the range 0.5 - 25 μm/s.

9:15 AM *J4.4/V5.4
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 (UV) 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 188 - 350 nm 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 the lower 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-crystalline films of silicon nitride, silicon dioxide and silicon oxynitride have been demonstrated. In this paper, UV-induced growth of high dielectric constant (tantalum oxide, titanium, or PZT) and low dielectric constant (polyimide and porous silicon) thin films by photo-CVD and CVD processes, as well as the effect of the low temperature UV annealing, are discussed. Film properties, determined using ellipsometry, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV spectrophotometry, scanning, transmission Electron microscopy (SEM), and electrical characterization, showed that good quality layers could be produced. Leaking current densities as low as 0.9 A/μm2 cm and 32 μA/μm2 cm have been obtained for the as-grown tantalum oxide thin films formed by photo-induced processing and photo-CVD, respectively - several orders of magnitude lower than for other similar films prepared by any other technique. A subsequent low temperature (400°C) UV annealing step improves these to 2 nA/μm/cm at 0.5 MV/cm and 7 μA/cm2 cm, respectively. These values are essentially identical to those only previously obtained for films deposited by alternative methods and annealed at temperatures between 800 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 J4.5/V5.5
LASER DIRECT WRITE OF CONDUCTING AND INSULATING TRACKS IN SILICON CARBIDE. Deepak Sengupta and Arwinda Kar, Laser-Aided Manufacturing, Materials and Micro-Processing Laboratory, School of Optics and Center for Research and Education in Optics & Lasers (CEROL), The University of Central Florida, Orlando, FL; Nathaniel R. Quick, Applicate 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 10–4 Ωcm were produced from insulating substrate with an initial resistivity of 10^11 Ωcm. 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, Human 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 characterization, semiconductor sensing, and electronic devices. The criteria for extending this technology to other ceramic bulk and thin film conformal surfaces will be discussed.

10:15 AM J4.6/V6.5
LASER GUIDE DIRECT WRITING. Robert Pastel, Peter Geiser, Edward Njugunda, Dept of Physics, Allan Smith, 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 microns. LGDW is a versatile and powerful tool for the construction of 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 performed on a variety of substrates. 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 particles 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.

10:45 AM J4.8/V5.8

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 a pulsed laser to transfer material from a donor ribbon onto an acceptor substrate with a feature size as small as 50 microns. The donor ribbon consists of a quartz wafer with a single side coated with a powder and/or a metallic or organic precursor of interest (metals, ferrites, ferroelectrics, etc.). The transfer efficiency and resolution have been determined as a function of the ribbon manufacturing 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 = 308 nm) was focused down to average spot sizes ranging from 10 - 50 microns with fluence ranging from 0 to 100 J/cm2 . The laser pulse rates between 2 - 20 Hz. Glass, alumina, dural 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 formations. Thin film capacitors, resistors, conductors and devices were written on the mesoscopic scale successfully. In-situ and ex-situ annealing of the
transferred materials was performed by both pulsed Nd: YAG laser (1.06 microns) and conventional furnace heat treatments at 250°C to increase the substrate adhesion and to transform the Jay Alumina into a HP 4291B Impedance Analyzer.

11:15 AM 34.9/V.5.9

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

Parmod is a family of materials that 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 single-step process eliminates the hazardous waste and employee health & safety issues associated with conventional photolithographic photolithography. Recently, the Parmod technology has been extended from metals to oxides to enable printing passive electronic components such as resistors, capacitors, and interconnects as well as 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 34.10/V.5.10

NUMERICAL SIMULATION OF LASER INDUCED SUBSTRATE HEATING FOR DIRECT WRITE OF MESOSCOPIC INTEGRATED CONFORMAL ELECTRONICS (MICE) Sam Lowry, Sundip Mianmder, J.C. Sheu, CFDR, Huntsville, AL; Robert Stewert, CMS Techntronics 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 Techntronics 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 FID code to predict the conductive, convective, and radiative 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, showing simulations work along with empirical validation. The capabilities, limitations, and potential applications of the model with respect to MICE are discussed.

11:45 AM 34.11/V.5.11

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. Fien, J. Leblan, P. McGinn, J. Thompson, Department of Chemistry, University of Dundee, Dundee, UNITED KINGDOM; W. Shahk, Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UNITED KINGDOM.

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 from 15 to 100°C and in various 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 annealed temperatures on metal films deposited by a direct write method.

SESSION 15: LASERS IN MICROMACHINING AND SURFACE MODIFICATION

Chair: Dr. Paul D. Norton and Dr. John McNary

Wednesday Afternoon, April 26, 2000
Nob Hill C/D (Marriott)

1:30 PM 35.1

LASER-ASSISTED MATERIALS PROCESSING. Chris B. Schaffer, André Broduie, José F. García and Eric Namn, Harvard University, Department of Physics and Division of Engineering and Applied Sciences, Cambridge, MA.

By focusing femtosecond laser pulses with high numerical-aerture microscope objective, we observe optical glass using energies that are in the range of unsimplified laser oscillators. When a femtosecond laser pulse is tightly focused inside a transparent material, energy deposition occurs only at the focus, where the laser intensity is high enough to cause photophysical processes. When enough energy is deposited, a localized change in the index of refraction is produced, i.e., the material is damaged. By scanning the focus through the sample, very precise, three-dimensional microstructures can be achieved. The diameter of the single shot damage spots is less than 0.5 mm. We have investigated the dependence of the damage threshold and morphology on the numerical aperture of the microscope objective, the wavelength of the laser, the bandwidth of the material, and the energy of the laser pulse. The potential of this technique for producing technologically-relevant structures such as waveguides and Bragg gratings, as well as the advantages of micromaching with only an oscillator instead of a complicated, expensive amplifier chain, will be discussed.

2:00 PM 35.2

MICROSTRUCTURING OF POLYMERS USING LIGHT-CONTROLLED MOLECULAR MOTORS. Céline Forien, Christine Denis, Paul Raimond, Jean-Michel Nanu, LETI-CEA Saclay, Organic Devices Group, Gif-sur-Yvette, FRANCE.

A challenging issue in the field of designing devices for photonic applications is to achieve a complete structuring of the materials. In the case of molecular materials, it involves the ability to have a full control of the molecular order. Anisotropic polymers have been shown to offer interesting prospects for material engineering using light matter interactions. It is now well-established that following excitation and cis-trans isomerization, thermal diffusion enables molecular rotation within the matrix leading finally to the cis-trans isomerization of the molecular isomer. Actually, such phenomenon was applied to all-optical polar ordering. More recent results on photoinduced surface-relief gratings have also opened the way to new transport control using optical fields. It was shown that irradiation of such materials with an interference pattern of coherent light could induce not only an alignment of the chromophores throughout the volume of the material but also a controlled modification of the film surface, in conjunction with the light interference pattern. Several explanations were proposed. We give experimental evidence that together with the surface-relief-grating formation, a chromophores concentration gradient could also be simultaneously evidenced. Both results indicate that the surface-relief-grating formation obviously follows chromophore migration from high intensity to low intensity regions, photoinduced molecular movements leading to polymer chain migration. We propose a simple model based on photoinduced amine-benzene diffusion in polymeric matrices following cis-trans isomerization. In view of our recent experiments, this model accounts qualitatively for the essential features of photoinduced surface-relief gratings. Deeper understanding of the relevant parameters of molecular translation processes is now a key issue for optimization of such an optomechanical effect. Interestingly, such photoinduced molecular-motor effects represent a promising route toward device micro and nano-structuring.

2:15 PM 35.3

PROCESS MODELING OF THE LASER IMMERSED SURFACE MODIFICATION OF CERAMIC SUBSTRATES FOR THERMAL AND ELECTRICAL LINES IN MICROSYSTEMS. Herbert Grund, Roland Heidinger, Magnus Rohde, Sabine Rüdliger, Forschungszentrum Karlsruhe, Institute for Materials Research I, Karlsruhe, GERMANY; Johannes Schneider, Karlsruhe Institute of Technology, Institute for Materials Science and Engineering II, Karlsruhe, GERMANY.

For many applications in microsystems technology the question of thermal and electrical requirements is of major importance. Today conducting paths between active elements on ceramic substrates are formed by lithographic methods. A possible alternative is based on the induced surface modification. The advantages are an easy design and a good bonding to the substrate. By adding laser pulses in a different thermal or electrical conductivity into the laser melted paths the material properties of the ceramic substrate are changed. Two variants are differentiated: The injection and the precooling process.
Due to a minimal feedable particle size homogeneous conducting paths generated by the injection process are limited down to a line width of 88 µm. For the injection preforming the ceramic material was carefully cut and a line width down to 0.2 mm was achieved. The primary ceramic substrate material is Cordierite because of its outstanding properties such as low thermal expansion and good thermal shock resistance. Modeling the various aspects of the modification process was sought to provide selection and control of process parameters. For the first step the thermal profile during laser induced surface melting was calculated using the finite element method. Both, contact is most responsible for the modified line generated lines. This behaviour was approached by the assumption of an anisotropic thermal conduction geometry. For alumina as reference material the simulation successfully describes the experimental results in terms of line width and depth which depend on laser power density. On the other side the assumption can not describe satisfactory both convection in Cordierite. Therefore a new model will be developed using the fluid dynamic program FIDAP.

3:00 PM 15.4 VUV EXCIMER LASER ABLATION OF ORGANIC MATERIALS AND METALS: MECHANISMS AND APPLICATIONS. M. Koch, M. Koch, M. Lapp, K. Mueller, G. Pleule, M. Stuke, Institute of Surface Physics, University of Hamburg, Germany.

Monterotondo The small penetration depth of 1.57 nm gives a light organic materials implies low threshold removal with high efficiency often exceeding 1 monomer/photon. In addition, some materials containing PMMA, ultra-thin layers, and submicron microchannels can be ablated using femtosecond pulses in high-power density regions. Laser ablation with short laser pulses reduces thermal penetration effects during pulse duration. Information on the -thermal- mechanism of the high efficiency removal process can be obtained via time-of-flight diagnostics in a laser mass spectrometer [3]. Recent results on 15 nm ablation of liquid mercury will be presented. [1] G. Pleule, M. Lapp, M. Stuke, MRS Proc. 544 (1999) 3-8

3:30 PM 15.5 LASER MICROMACHINING OF METALLIC MOLD INSERTS FOR REPLICATION TECHNIQUES. Wilfried Pleiding, Andreas Meier, Thomas Heinemann, Herbert Grahn, Kersten Zun-Gür, Forschungszentrum Karlsruhe GmbH, Institute for Material Research.

The rapid manufacturing of mold inserts for micro injection molding is realized by laser micromachining of cemented carbides, alloy or carbon steel. The structure of cemented carbides is performed with Q-switch Nd:YAG laser radiation. During the laser beam interaction a selective evaporation of cobalt binder phase occurs. A porosity in the side walls of polishing the surface is detected. Additionally, a recrystallization layer is formed on the laser treated surface. With increasing laser power the surface roughness Rq of the reaction layer increases from 2 µm up to 6 µm. After wet chemical etching Rq decreases down to 1.2 µm, and this seems to be independent of the used laser power density. Excimer vaporization is used for further improvement of surface quality. After an incubation period of 2 minutes a laser assisted dry etching process is initiated with etch rates of about 0.2 mm/minute. The resulting surfaces reveal a roughness of about 300 nm with no pores at the side walls. The Laser Micro Caving (LMC) of steel is performed with cw Nd:YAG laser radiation. LMC enables a clean patterning process with only a small amount of debris and melt. During LMC of Steel a recrystallization layer is formed on the surface. An oxide surface layer can be observed. The formation of these reaction layers as well as the etch rate and the surface quality strongly depend on the chemical composition of the steel and the process parameters. The laser generated temperature field is calculated with a finite element model in order to improve the patterning results by optimizing the process strategy. Mold inserts are manufactured by laser patterning, and microstructures composed of polymers or ceramic microstructures can be successfully produced by using the RIM technique with aspect ratios up to 10 and a minimum surface roughness of Rq=300 nm.

3:45 PM 15.6 QUANTIFICATION OF MOLTEN EJCTION PHENOMENA DURING LASER DRILLING. K.T. Voisey, C.F. Cheng, T.W. Clyne, University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

During laser drilling, material removal in general occurs both by vaporization and by the expulsion of molten material. The latter constitutes 98% of the rapid build-up of gas pressure within the growing cavity as evaporation takes place, but the precise mechanism responsible for the phenomenon is still unclear. The current work is aimed at gaining an insight into these mechanisms via measurement of the fraction of molten material ejected from molten cavities during laser drilling under different conditions. Attention is first devoted to the issues which need to be considered when making experimental measurements of the fraction of molten removed by melt ejection. This includes the collection efficiency and the possibility of chemical changes occurring during the process. Results are then presented from work with a range of metallic substrates (milk steel, tungsten, lead, copper, aluminum, and nickel superalloys), drilled with a JPT® Nd:YAG laser under different conditions. Observed variations in the melt ejection levels are considered in terms of the expected effects of certain material property values and the mechanisms of melt ejection. The development of an existing finite difference heat flow model for laser drilling so as to incorporate the melt ejection phenomena is explored in the light of these results.

4:00 PM 15.7 SURFACE PROCESSING AND MICROMACHINING OF POLYMIDE DRIVEN BY A HIGH AVERAGE POWER INFRARED FREE ELECTRON LASER. Michael J. Kelley, Dept. of Applied Science, College of William & Mary, Williamsburg, VA and Thomas Jefferson National Accelerator Facility, Newport News, VA.

The long history and wide use of polyimide as a dielectric in the microelectronics industry has made it a favorite material for laser processing. The PELI used in the present work delivered picosecond–long 25 microjoule pulses, at approximately 3.10 and 5.85 microns. The former is away from any significant absorption band, while the latter is at the strongest band in the IR: this study explored laser drilling and surface modification of un- and aluminized DuPont Kapton PMDA-ODA film.

4:15 PM 15.8 MICROSTRUCTURAL CHARACTERIZATION OF ELASTOMER/CARBON COMPOSITE ABLATED WITH KrF EXCIMER LASER. Jean-François Silvain, Hiroshi Niino, Akira Yabe, Institute of Materials Science Condensed Matter at the University of Bordeaux, French CNRS, University of Bordeaux, France. National Institute of Materials and Chemical Research (NIMC), Tsukuba, Japan.

Excimer laser ablation of elastomer composite containing carbon black produced conical microstructures on the ablated surface upon irradiation with the second harmonic of Nd:YAG laser. Nowadays, it is well known that excimer laser ablation of polymers can yield a variety of morphological changes such as conical, granular, ripple, cone-like structures, and so on. The ablated surface of microstructures plays an important role, for instance, for improving adhesive bonding, controlling friction and wear, fabricating filtration, or aligning liquid flows. In particular, we are interested in surface modifications of elastomeric composite materials by laser ablation, because the control of tribological properties such as friction and wear is directly correlated with microstructures on the surface as one of the most important factors. Based on studies by scanning (SEM) and transmission electron microscopy (TEM), the mechanism for the conical structure formation was discussed. Before laser irradiation, optical microscopy observation on thick TEM foil shows agglomeration of carbon micrometric particles (expanded shells whose thickness is around 5 to 10 µm) and which are between 40 to 80 µm long oriented perpendicular to the material surface. Cone-like structure formation during KrF excimer laser ablation is associated with the diffusion and aggregation of micrometer carbon particles on the top of cone like structures and with the depletion of expanded carbon shells inside the molten area. Growing mechanism of the layers will be presented and followed up to aggregate small cone-like microstructures in a thick molten layer upon repeated laser irradiation.

4:30 PM 15.9 EFFECTS OF EXCIMER LASER IRRADIATION ON MICROMACHINING OF GLASSES. Pin Yang, Eugene L. Venturini, Gilbert L. Benaimides, Sandia National Laboratories, Albuquerque, NM.

Glass, due to its chemical inertness, optical transparency, and low cost, has become the material of choice for many optical diagnostic microstructures. Moreover, the use of laser ablation to make micromachined glass is difficult to create high aspect ratio features required in the microsystems through a conventional wet process or a plasma etching technique. Excimer laser ablation has demonstrated to be an effective method to create micro-features on glass without causing large collateral thermal damage. In this study we will report the
micromachining ability of different three glasses, including quartz, pyrex, and soft glass, using a 248 nm wavelength excimer laser. Defect density created by UV ablation and irradiation for different glasses will be characterized. A correlation between the defect density, UV absorption, ablation threshold, and micromachining ability will be reported. Sandia is a multi-program laboratory operated by Sandia Corp., a Lockheed Martin Company. Department of Energy under Contract DE-AC04-54AL08500.

4:45 PM J5.10
ABSORPTION OF LASER DAMAGED FUSED SILICA.

Laser damage on fused silica grows even if the initial absorbing defect is removed. The optical properties of the damaged material control growth upon repeated irradiation. Enhanced absorption at laser-damaged sites is involved with the damage growth. The implications of absorption and electric field enhancement at damaged sites for laser damage growth are discussed.

SESSION J6U8: JOINT SESSION
LASER-BASED DEPOSITION OF OXIDES
Chair: P. Naylor
D.O. Perkins
Thursday Morning, April 27, 2000
Nob Hill (Marriott)

8:30 AM *J6.1/U8.1
ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION OF THIN FILMS. V. Crician and B.K. Singh, University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

Pulsed laser deposition (PLD) has emerged as one of the most promising techniques for growing thin films due to several important advantages such as the use of a relatively low substrate temperature. For many applications, a further reduction of the process temperatures is highly desirable to prevent harmful film and/or ambient gas-substrate interaction, unwanted substrate interdiffusion processes, and sublimation of volatile components. Unfortunately, most high quality PLD grown materials still require substrate temperatures above 500°C. If the laser pulse temperature on the substrate without sacrificing the crystalline quality, stoichiometry, and film properties, then a non-thermal source of energy and a more reactive gaseous atmosphere should be used during growth. Laser-assisted PLD, a process where either a part of the incoming laser pulse used for ablation or a second laser pulse is used to irradiate the growing film showed great promise. However, this technique is rather expensive due to the use of a second laser source. The pulsed beam can induce appreciable heating of the outermost surface of the substrate, thereby precluding its application to sensitive substrate materials such as plastics. Moreover, optical interference effects when the growing film is very thin can further complicate this process. A novel version of this technique, where the second laser is replaced by an inexpensive low-pressure Hg lamp is presented here.

The short wavelength UV radiation (185 nm) emitted by such lamps can dissociate molecular oxygen to form atomic and atomic oxygen. In addition, to enhance the PLD process, the UV lamp can be used during the cooling stage as well. We have investigated the microstructure and properties of several oxide and nonoxide thin films grown by UVPLD technique at moderate temperatures and compared them with those obtained from films grown using conventional PLD under similar conditions.

9:00 AM J6.2/U8.2
EPITAXY OF OXIDES ON DISSIMILAR SUBSTRATES USING PULSED-LASER DEPOSITION. David Norton, Chan Peng, Yong Lee, John Baidi, Stephen Peasyock, Gyuha Eres and Matthew Chisholm, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

The integration of electronic oxide materials on semiconductor and metal substrates is important in numerous applications. Crystalline oxides on semiconductors may be used in the fabrication of future generation metal oxide-semiconductor device structures. Epitaxial oxides on metal are key elements in the development of emerging superconducting wire technologies. In both cases, the formation of epitaxial oxide structures is both enabling and complex. One must consider both the kinetics of film growth on a dissimilar material, as well as the thermodynamic stability of the oxide/non-oxide interface. In this talk, we will discuss the role of plume kinetics and thermodynamics in the formation of epitaxial oxide films on semiconductors and metals using pulsed-laser deposition. The specific cases to be discussed include CeO2 on [001] Ge and [001] Ni. Reflection high energy electron diffraction is used to characterize the nucleation of ceria on these surfaces. Z-contrast STEM will be used to characterize the epitaxial interface. High resolution four-circle X-ray diffraction will be used to characterize the epitaxial relationship between the film and crystalline substrate.

This research was supported by the U.S. Department of Energy under contract NO. DE-AC05-86OR22644 with Lockheed Martin Energy Research Corp.

9:15 AM J6.3/U8.3
1Department of Materials Science and Engineering, University of Florida, Gainesville, FL; 2Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, 3North Carolina A&T State University, Greensboro, NC.

The fabrication of MgO/3Cu/MnO3 (LCMO) thin films on silicon (Si) substrates is very important from the point of view of integrating colossal magnetoresistive films based memory devices with Si for the next generation magnetic random access memory (MRAM) technology. A direct growth of LCMO films on Si, however, is hindered by lattice mismatch and chemical reaction between the film and the substrate materials. It is in this context that we have tried to grow LCMO film on Si by using a highly conducting barrier layer of TiN, which has emerged as an attractive material because of its low electrical resistivity and its excellent mechanical stability and reliability when subjected to high temperatures. By suitably changing the growth parameters during pulsed laser deposition, TiN films with resistivity as low as 20-50 µΩ-cm were obtained. In order to achieve epitaxial growth of LCMO films, MgO and SiO2 films were used as intermediate layers between LCMO and TiN layers. The structural characterization of single layered and multilayered structures were carried out using x-ray diffraction, transmission electron microscopy, and photoluminescence measurements. The magnetic and magnetoresistance properties of LCMO films on Si were examined in the range of 10-300 K using superconducting quantum interference device magnetometer. The results have indicated that the properties of LCMO films on Si substrates, deposited under optimized condition, are on par with the properties of LCMO films on conventional oxide substrates such as LaNiO3 and SiO2 in terms of paramagnetic to ferromagnetic transition temperature, insulator to metallic transition temperature, and magnetoresistive response ratio. The magnetoresistance and magnetic properties of LCMO films in addition to a structural model explaining the epitaxial growth of LCMO films on Si.

9:30 AM J6.4/U8.4
PREPARATION OF PZT/YBCO HETEROSTRUCTURE ON YSZ COATED Si BY KF LASER ABLATION. Kenji Ebihara, Fumiko Mitsugi, Tomoko Ikeyami, Kumamoto University, Department of Electrical and Computer Engineering, Kumamoto, JAPAN; Jagdish Nath, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC.

Kf excimer laser ablation technique is applied to fabricate the ferroelectric Pb[001], PZT, and YSZ/MgO(100) substrate. The YBa2Cu3O7-δ (YBCO) bottom electrode was deposited on the coated by YSZ buffered layer under the appropriate deposition conditions. Laser fluences up to 1 J/cm2, atmosphere pressure 100-200 mTorr, substrate temperature 650-710°C. The plasma plumes during film preparation were studied using ICCD images. The fabricated PZT/YBCO/YSZ/Si capacitor shows the ferroelectric properties of the remanent polarization 26 µC/cm2 and the coercive force 31 kV/cm which are comparable with the results of the PZT/YBCO/MgO(100) capacitor. The switching fatigue for this sample has been investigated to be 10^10 cycles for the decrease to 10 µC/cm2 polarization.

9:45 AM J6.5/U8.5
PULSED LASER DEPOSITION OF EPITAXIAL SrO2 FILMS ON [100]LaNiO3 AND [100]Si. P.W. Yang and K.H. Wong, Dept of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR CHINA.

Thin films of SrO2 have been grown on [100]LaNiO3 and TiN buffered [100]Si substrates by pulsed laser deposition. The films were deposited in ambient temperature range of 450°C - 700°C and under ambient oxygen pressure between 10^-5 and 10^-2 Torr. Their structural properties were characterized using a four-circle x-ray diffractometer. High quality SrO2 films were obtained at growth temperatures above 500°C without post annealing. The epitaxial relationship of SrO2 films on [100]SrO2/[001]LaNiO3 and [100]SrO2/[100]TiN was observed for films deposited at ≥ 550°C. X-ray photoelectron spectroscopic studies of the films suggest that the vacuum cleaning is mainly responsible. Charge transport measurements show that the films vary from semiconducting to highly conducting for
different growth conditions. Resistivity of a few micro-ohm cm was recorded for some of the epitaxial SrVO$_3$ films.

10:30 AM *J6.6/US.6* IMPOSED LAYER-BY-LAYER GROWTH OF COMPLEX OXIDES WITH PULSED LASER INTERNAL DEPOSITION. Drew H. Boot, Robert W. Butts, and Michael J. Rotska, University of Twente, MESA+ Research Institute, Applied Physics, THE NETHERLANDS.

In oxides electronics the control on an atomic level becomes a central issue. The interface in gate-oxides, electrical, and magnetic junctions has to be controlled with the utmost precision. In order to be able to create a crystal structure by depositing consecutive unit cell layers of different materials, a layer-by-layer growth mode is a prerequisite. nucleation of each next layer may only occur after the previous layer is completed. We introduced a growth method, based on a periodic sequence: very fast deposition of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the film can recognize. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where otherwise island formation would dominate the growth. We present the results obtained for homo- and hetero-

epitaxial growth on SrTiO$_3$ as monitored by high-pressure RHEED. In addition, Monte Carlo simulations are used to support the applicability of interval deposition. Furthermore, this technique is used to grow superconducting as well as ferrromagnetic junctions.

11:00 AM J6.7/US.7 GROWTH OF ZnO/MgZnO MULTIPLE QUANTUM WELL SUPERLATTICES ON SAPPHIRE BY PULSED LASER DEPOSITION. J. Neumayer, nasal University, Department of Materials Science and Engineering, Raleigh, NC; J. F. Muth, C. W. Teng, R. M. Kolbas, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC.

We have recently grown high quality Mg$_{x}$Zn$_{1-x}$O alloy single crystal films on sapphire substrate by pulsed laser deposition (PLD). The bandgap of these alloys was varied up to 4.27 eV by varying Mg content (x) from 34 to 54%.

Photoluminescence (PL) spectrums from these films obtained at room temperature were very bright characteristic of excitonic nature of emission. This new materials system opens up new possibilities for optoelectronic devices such as monolithic solar blind detectors and uv lasers. In further pursuance of this material system, we have grown ZnO/Mg$_{0.25}$Zn$_{0.75}$O multiple quantum well superlattices on sapphire by PLD. The well thickness was varied from 3.6 to 5.4 and the barrier thickness was kept constant in these heterostructures. The characteristics of these superlattices were performed by high resolution transmission electron microscopy, transmission measurements and photoluminescence. In optical transmission measurements, the features corresponding to quantum wells were resolved as two excitonic peaks of ZnO blue shifted as the well thickness decreases. The photoluminescence from these wells was excitonic and blue shifted from the corresponding ZnO band-edge PL value. The result is in agreement with the simple calculations performed assuming a band offset 0.5 eV between ZnO and MgZnO. The PLD has been successfully employed to achieve these ultra-thin layers with sharp interfaces. This work has a potential for fabricating high efficient opto-electronic devices based on ZnO.


11:15 AM J6.8/US.8 SINGLE QUANTUM WELL STRUCTURE OF MgZnO/ZnO/MgZnO ON C-PLANE SAPPHIRE. Sayab Chongun, Dan Chink, Wei Yang, R.D. Vispute, S.B. Ogale, K.P. Shun and T. Venkatesan, Ceramics, Dept of Physics, Univ of Maryland, College Park, MD.

The single quantum well structure of MgZnO/ZnO/MgZnO were grown on c-plane sapphire substrate by pulsed laser deposition. Photoluminescence measurement was performed on samples as a function of the well width. The quantum well width was varied by adjusting the deposition time of ZnO content. The sheet resistance was measured by four-probe method when the well width was decreased. These results were fitting with calculation based on simple square well model using effective mass of electron (0.41) and hole (0.57). By eliminating the well width parameter, the well width is quantized and the potential of band offset has been obtained. This quantized-energy and the well width as a function of band offset, growth conditions, interface roughness, quantum size effect on MgZnO/ZnO/MgZnO quantum wells will be discussed.

11:30 AM J6.9/US.9 DEVELOPMENT OF LSCO AND LNO OXIDE ELECTRODES FOR SENSOR PROTECTION DEVICES. Mani Chunchong, Kelly Baker, D. K. Fischer, D. B. Rutledge, M. H. R. Butler, University of Cincinnati, Department of Ceramic and Materials Engineering, Cincinnati, OH.

Oxide electrodes play a key role in a variety of devices, including pyrometric schemes for sensors that operate in the 3 - 5 mm and 8 - 12 mm ranges. One such protection device currently under development is an electrostatic shutter, which is driven into a closed position for protection against high energy pulses. For the fabrication of this device, electrodes must be developed that possess a sheet resistance of 300 to 500 Ω/sq. and which have a transparency, ideally, of at least 80%. We are evaluating the suitability of (La,Sr)CoO$_3$ (LSCO) and LaNiO$_3$ thin films for this application by attempting to achieve the appropriate balance between transparency and conductivity through control of the extent of crystallization, oxygen stoichiometry, composition, and thickness. Films are deposited on both BaF$_2$ and MgO substrates by sputtering or solution deposition followed by annealing at temperatures as high as 1100°C. Crystallization into the perovskite structure has been studied by x-ray diffraction and optical properties have been studied by standard FTIR techniques. As expected, both the conductivity and transparency of the films are highly dependent on the heat treatment conditions. For the solution deposited films, heat treatment temperatures in the range of 700 to 800°C are required to fully crystallize the perovskite structure. For films that are approximately 150 nm in thickness, calculations of the extinction coefficient of the LSCO coated materials indicated an average band gap approach 150,000 cm$^{-1}$ for films heated at 800°C. Measurements of the resistivity of films fabricated under the same processing conditions indicate that values of 500 µΩcm may be obtained. These results suggest that it should be possible to achieve the required sheet resistance and transparency for the development of the electrostatic shutter. However, target film thickness will be in the range of 15 - 25 nm.


Textured and epitaxial ZnO films are grown on GaAs and sapphire by pulsed laser deposition (PLD). They are compared to understand the differences in crystal properties. Crystal qualities for ZnO films are studied by atomic force microscopy (AFM), x-ray diffraction (XRD), and photoluminescence (PL). Optical qualities for textured ZnO films are remarkably excellent, comparable with those for high-quality epitaxial ZnO films grown on sapphire. Textured ZnO films show very strong and narrow bound exciton peaks. These results will be discussed.

SESSION J7: PULSED-LASER DEPOSITION
Chair: Clinton B. Lee and Xinliao Xi
Thursday Afternoon, April 27, 2010
Salon 10/11 (Marriott)

1:30 PM J7.1 RECENT ADVANCES IN THE PULSED ENERGY DEPOSITION OF COMPOUND MATERIALS. T. Venkatesan, University of Maryland, Department of Physics and Electrical Engineering, College Park, MD and Necnica, Inc., Beltsville, MD.

In this review I will address both material/device issues related to pulsed energy deposition of materials as well as deposition system advances. On the materials front pulsed laser deposited (PLD) wide band gap materials such as AlN have become very important in the fabrication of high power devices based on SiC. Using PLD AlN as a dielectric MOSFET devices on SiC have exhibited world record leakage currents at temperatures as high as 450°C. Using PLD deposited PZT and CMR heterostructures non-volatile memories have been made which show order of magnitude on/off resistive ratios at operating voltages of only ± 6 Volts. At the system front, a black body heater developed for PLD is shown to make five 2 double sided high temperature superconducting films simultaneously. Lastly, pulsed electron beam deposition (PED) is compared with PLD as a compatible low energy to high energy scheme for operating the PED singly or in conjunction with PLD will be discussed.

2:00 PM J7.2 CARBON NANOTUBE FILMS SYNTHESIZED BY COMBINED LASER NITRIDE AND ION BEAM PROCESSING. Z.Y. Chen, J.P. Zhao, T. Yano, T. Oiso and M. Yoneda, Shinagawa National Industrial Research Institute, Takeyama, JAPAN.
Carbon nitride films have been prepared by laser ablation of a graphite target in nitrogen gas beam at 1 atm. The processing parameters of laser fluence and ion beam voltage were varied along with substrate temperature. The composition and microstructure of the resultant films were characterized by Rutherford back-scattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and micro-Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). The average nitrogen content of carbon nitride phase was ~50% and the films were found to be essentially amorphous. XPS analyses indicated that the films consisted of two carbon nitride phases. One phase had a stoichiometry of 1.3 (N:C) which was near that of C-N=C and was identified as the α-CN component. The other phase had a stoichiometry of 0.2 which was equal to that of C=H and was identified as predominantly an sp²-hybridized structure. XRD pattern showed the coexistence of α- and β-C3N4 in films. FTIR observed the presence of bands between 1500 cm⁻¹ and 1700 cm⁻¹. All nitrogen were C-N, C≡N, C≡N together with a little amount of C≡N, which was in agreement with XPS analyses. The bonding state was strongly influenced by deposition condition, especially the nitrogen and carbon arrival ratio. A significant amount of disorder was present in all of films, as indicated by TEM and micro-Raman analysis. High deposition temperature favorable to CN phase but will reduce the nitrogen content and induce graphitization of C-C phase. Low ion energy, suitable nitrogen and carbon arrival ratio, and optimized laser fluence will promote the formation of C-N=C.

2:15 PM 17.3
MECHANICAL PROPERTIES OF HARD COATINGS SYNTHESIZED BY LASER ABLATION METHOD
Ashish Kumar, M. Vedavyas, Department of Electrical Engineering, University of South Alabama, Mobile, AL, M. Sherif, Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL.

The development of superhard coatings with high level of hardness, wear resistance and toughness is an important area of research with numerous applications. Current research is focused on the development of carbide and nitride coatings by the Pulsed Laser Deposition (PLD) method. Thin films consisting of carbides (titanium carbide, silicon carbide and boron carbide) and nitrides (titanium nitride, silicon nitride, and aluminum nitride and carbon nitride) were deposited on Si(100) substrates using PLD method. The structural and microstructural properties of these films have been characterized using x-ray diffraction, scanning and transmission electron microscopy techniques. The mechanical properties of the films were evaluated to measure the hardness and modulus values. Microhardness made of alternate layers of TiN and TiB2 films is likely to offer promises of exceptionally high hardness and moduli and, therefore, can be employed for future protective coatings. Single layer of TiN, TiB2 and TiB2/TiN microlaminate coatings with varying thickness were initially deposited on Si(100) and oxidized Si(111) substrates by pulsed laser deposition techniques and then characterized by x-ray diffraction, transmission electron microscopy and nano-indentation methods. Analysis of the results showed that the elastic modulus and hardness of this multilayer structure is expected to be lower than their corresponding monolithic coatings of either of the two constituent films. It is suggested that the smooth nature of the interface between TiN and TiB2 is responsible for the improved hardness. This work was supported by NSF-DMR-0901899 grant.

2:30 PM 17.4
OPTIMIZATION OF THE PROCESSING PARAMETERS FOR PULSED LASER DEPOSITION OF NICKEL SILICIDE OHMIC CONTACTS ON SiC

This research investigates the potential of pulsed laser deposition to create reliable high current ohmic contacts of NiSi on single crystal 4H-SiC. Since this nickel silicide is the stable interphase in the nickel-silicon carbide diffusion couple, direct deposition eliminates the need for post deposition high-temperature (1000°C) annealing treatments needed in complex multi-component contacts. This study examines the processing parameters that must be used during deposition to obtain the desired microstructural characteristics for the contact. Pulsed laser deposition of nickel silicide produces smooth films with an amorphous or nanocrystalline structure that is interrupted by the presence of macropores. Macropore formation on the resulting films appears in the form of solidified droplets of the eutectic composition (Ni-Si) that form during the ablation event. The dependence of the number and size distributions of these droplets on laser fluence and background gas is examined.

3:15 PM 17.5
ADVANCES IN THE GROWTH OF ORGANIC THIN FILMS USING THE MATRIX ASSISTED PULSED LASER EVAPORATION (MAPLE) TECHNIQUE

Thin organic films play an important role in next generation electronic devices, passivation coatings and chemical and biological sensors. New methods to process organic thin films over large and small areas, homogeneously, with smooth surface morphologies, and to achieve controlled and precise thickness, are required for improved performance and component size reduction. NRL has developed a novel approach to process polymer and large organic biocatalysts thin films called MAPLE, for matrix assisted pulsed laser evaporation. The MAPLE technique is carried out using pulsed laser ablation of a polymer sample in a matrix gas while depositing a pulsed laser beam (1064, 213 and 268 nm; fluence = 0.01 to 0.5 J/cm²) onto a frozen target (100 - 200 K) consisting of a soluble polymer or organic compound dissolved in a solvent matrix. The laser beam evaporates the surface layers of the target, with both solvent and solute molecules being released into the chamber. The volatile solvent is pumped away, whereas the polymer/solvent molecules coat the substrate. This uniform films (~1000 nm) of various materials, such as chemoselective polymers, biodegradable polymers, polymer composites and carbohydrates, have been deposited over numerous types of substrates. The films prepared using this method have been examined by optical microscopy, scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, and electrophysiology mass spectrometry. Careful control of the processing conditions allowed the complex polymer/solvent molecules to be transferred to the substrate in uniform films without any significant chemical modification. Using MAPLE, large or small regions within a substrate can be discretely coated with submonolayer thickness control. Coatings prepared by the MAPLE technique have been used in the fabrication of chemical sensors. These MAPLE coated devices have surpassed the performance of identical sensors coated by traditional techniques.

3:45 PM 17.6
OPTIMIZATION OF PROCESSING PARAMETERS FOR DEPOSITING HYDROPHILIC POLYMER FILMS BY PULSED LASER DEPOSITION
James D. Talley, James Fitz-Gerald, Rajiv Singh, University of Florida, Gainesville, FL.

Surface modification / functionalization of biomedical devices has gained significant interest in the last decade to improve the tissue interactions and cellular response of the implant surface. Biomedical devices such as stents, catheters, tissue implants, and contact lenses could benefit significantly from improved tissue response. Deposition of biodegradable polymers such as poly([L-lactic acid]) (PLLA), poly([D,L-lactic acid-co-glycolic acid]) (PLGA), and poly([ethylene glycol]) (PEG) and non-biodegradable polymers such as cross-linked poly(ethylene glycol) (PEG) and poly(vinyl pyrrolidone) (PVP) have been investigated. Optimization of the process parameters using a Pulsed Laser Deposition (PLD) technique controlled by SEM, GPC, LC/MS/MS, NMR, and FTIR. Deposition of polymer films showed improved morphological properties and higher molecular weights slightly above threshold laser energies, with increased penetration depth and decomposition occurring at roughly twice the threshold energy. General compositional peaks using FTIR and NMR verified deposited polymer films molecular structures and decomposition products, while GPC was used to obtain relationships between energy density and deposited polymer molecular weight. Finally, identification of polymer and decomposition products was performed using LC/MS/MS. Overall, this PLD coating technique has several unique advantages over other techniques including [1] fast prototyping on the order of minutes, (2) flexibility in depositing a variety of materials such as various polymers and composite coatings, (3) control of coating thickness, morphology, molecular weight, and structure of desired films.

4:00 PM 17.7
PREPARATION OF SUPERHARD FUNCTIONALLY GRADED TETRAHEDRAL AMORPHOUS CARBON COATINGS BY PULSED LASER DEPOSITION (PLD)

The internal compressive stress as large as 10 GPa has been the major stumbling block for preparation of relatively thick superhard tetrahedral amorphous carbon (TaC) films. We have successfully deposited Ta-C films as thick as 1000 nm by mechanical doping to
reduce and alleviate the level of internal compressive stresses. In this paper, we have prepared functionally graded TaC coatings by pulsed laser deposition. The thickness of films of significantly improved adhesion was measured to be up to 1500 nm. The concentration of foreign atoms such as silver, copper, silicon and titanium was decreased away from the interface and the surface layer was pure TaC. Nano-indentation measurements were performed on the coatings. Nano-hardness as high as 65 GPa and Young's modulus as large as 600 GPa were obtained for the functionally graded TaC films. Micro-Raman measurements and microstructural analysis by transmission electron microscopy and electron energy loss spectroscopy was carried out to obtain information about the bonding environment and atomic structure of the coatings as a function of foreign atoms.

4:15 PM 17.8
CRYSTALLINE CHROMIUM CARBIDE THIN FILMS GROWN BY PULSED Nd:YAG LASER DEPOSITION. Kenyna Doi, Hirohara Kawasaki, Satoshi Hirashiki and Yoshihiko Sadam, Department of Electrical Engineering, Saisebo National College of Technology, Saisebo, Nagasaki, JAPAN.

Chromium carbide (CrCx) thin films have been grown on Si(100) substrates by a pulsed Nd:YAG laser deposition method. The effects of substrate temperature (Ts) and methane gas pressure (PCH4) on the properties of the CrCx thin films are discussed. Glancing angle X-ray diffraction (GXR) and a field-emission secondary electron microscopy (FE-SEM) show that the substrate temperature is one of the most important parameters in the fabrication of a crystalline chromium carbide film. The film prepared at Ts ≥ 600°C is a polycrystalline thin film composed of CrxC2 and CrxC3. This polycrystalline thin film can be prepared independent of PCH4. One of the growth mechanisms of the CrxC2 may be considered that the density of Cr atoms may be higher than that of C atoms in the plasma phase, and thus, the density of C atoms related to the surface reaction is higher than that of C atoms on the surface of the substrate.

4:30 PM 17.9
STRAIN AND OXYGEN STOICHIOMETRY EFFECTS IN Ln2.3Sr6CuO4+x THIN FILMS. Weidong Si and Xia Xin Xi, Department of Physics, The Pennsylvania State University, University Park, PA.

By growing SrLaCuO4 buffer layers of different thickness on SrTiO3 substrates, we were able to control the strain in the doped La2SrCuO4+x thin films deposited epitaxially on them. When grown in molecular oxygen atmosphere, the undoped and lightly-doped La2SrCuO4+x films were insulating under tensile strain, but as the strain was gradually changed to compressive, an insulator-superconductor transition occurred. It shows that epitaxial strain influences the insertion of interstitial oxygen into the Ln2SrCuO4+x films, which affects both hole doping and interlayer coupling. The best Tc of 44 K was obtained under compressive strain and using highly reactive ozone/molecular oxygen mixture. Tc of the Ln2-xSr6CuO4+x films as a function of Sr concentration was studied from undoped to over-doped region. We found that the Tc suppression at 1/8 doping is sensitive to the strain, but insensitive to the oxygen stoichiometry. The effect of epitaxial strain on structural phase transitions, phase separation, and charge stripes are under investigation.

4:45 PM 17.10
THE PREPARATION OF NOVEL ZEOLITE FILMS VIA PULSED LASER ABLATION. Sharon E. Hogue, Lisa Washmon, Ashley Scott and Kenneth J. Bakus, Jr., The University of Texas at Dallas, Department of Chemistry, Richardson, TX.

Thin films and membranes of nanorod/gold metal oxides have been prepared using pulsed laser ablation followed by a hydrothermal treatment. An excimer laser (Krf, 248 nm) has been employed to evenly deposit molecular sieves on both planar and non-planar surfaces ranging from silicon wafers to optical fibers. A vibrating substrate holder has been designed to coat small three-dimensional objects such as glass beads and catalyst particles. Results for the deposition of oriented films of zeolite UTD-1, MAPO-39 and MCM-41 on porous metal foils will be described. Zeolites such as UTD-1 require a UV absorbing guest molecule for laser ablation to occur which is a phenomenon we refer to as guest assisted laser ablation (GALA). Additional results for the growth of zeolite NaX, NaY, beta and silicate on various substrates will be presented. The application of these molecular sieve films in the areas of separations, catalysis, sensors and electrochromics will be outlined.