SYMPOSIUM J

Laser-Solid Interactions for Materials Processing

April 25 – 27, 2000

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SESSION J1: FUNDAMENTALS OF LASER DESORPTION 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 MANNERED 1-5 eV PHOTON MEETS A BIG 10 eV BANDGAP, WHAT HAPPENS? STUDIES OF LASER DESORPTION 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 'interactions'. We present recent experimental results on the physics and chemistry of laser induced desorption and emission of atoms, ions, and electrons from single crystals 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. Gyoowan Han, Electro-Optics Program, University of Dayton, Dayton OH; 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 plume. The target was ablated by two different laser radiation (λ = 532 and 266 nm). Angular dependencies of intensity and velocity of the charged particles ware obtained by Faraday cup measurement at various laser power densities. The most probable speed of the charged particles from the UV laser ablation was faster than that of from the visible laser ablation. The velocity distribution of the charged particles from UV ablation shows less angular dependence then 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. Hidehiko Nonaka, Tetsuya Nishiguchi, Yoshiki Morikawa, Masaharu Miyamoto, Shingo Ichimura, Electrotechnical Laboratory, Tsukuba, Ibaraki, 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 UV-laser ablation of solid ozone can produce a pulsed 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 sapphire substrate attached to a copper block which is cooled down to 30 K on a cryopump-head. The purity of the solid ozone is further improved by raising the substrate temperature above the boiling point of oxygen, a main impurity. Pulsed laser light from a KrF laser (248 nm) which hits the Hartley band of ozone lying from 200 nm to 300 nm with a maximum at ca. 250 nm is used to ablated 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/cm^2 and then it decreases probably because of decomposition of ozone. Gaussian fitting of the time of flight signals 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 2,600K at the highest power density available in the present experiment.

10:00 AM *J1.4
RECENT PROGRESS ON LASER SURFACE CLEANING. Y.F. Lu, W.D. Song, 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 damage. For dry laser cleaning, two cleaning models were established for removal of particles from substrate surfaces from the viewpoint of energy and force. For steam laser cleaning, a cleaning model was established for removal of particles from substrate surfaces with 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 thresholds. 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 acoustic, electric 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 ENERGY MODULATION IN THE CRYSTALLIZATION OF POLY-Si FILM ON STEPPED SUBSTRATE. Kee-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 thin 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 bridge 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 5000$\AA$ deep trench etch, has locally modulated energy distribution because the vertical wall of the trench is exposed to relatively weaker 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 motivated 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 5000$\AA$ deep trench of gate electrode pattern of TFT, was formed in the oxide. Then a-Si film was deposited by PECVD at 320°C on the pattered 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 1000$\AA$ to 3000$\AA$ 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 random nucleation was suppressed because the temperature gradient in the molten silicon layer promoted lateral grain growth. In addition, a-Si remained as deposited on the lowest-temperature vertical trench wall. The remaining a-Si region can be used as an offset between poly-Si channel and drain of TFT in order to suppress large leakage current of poly-Si TFT.

10:45 AM J1.6
SIMULATION OF POLYCRYSTALLINE SILICON GROWTH BY PULSED EXCIMER LASER ANNEALING. Toshio Kudo, Daiji 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 substrates[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 propriety of Ichishima model was confirmed: the simulation results reproduced the super lateral growth (SLG) phenomenon observed experimentallly in the near-complete melting region[4)]. Under the strong fluctuation of Si grain size on energy density in the near-complete melting region, however, 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 delay time jitter, beam overlap ratio, 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, J. Lumin. 30 (1985) 395. 3) D. Ichishima 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 *J1.7
FABRICATION AND PATTERNING OF LARGE FREE-STANDING GaN SUBSTRATES BY LASER-INDUCED LIFTOFF.
Oliver Ambacher, Mike Kelly, Claudio Miskys, Lutz Hoppel, Christoph Nebel 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 foreign substrates is detrimental to the quality and function of the semiconductor. Numerous threading dislocations are generated in the epitaxial film to accomodate 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 high growth temperature. The use of a sapphire or silicon carbide substrate also complicates processing steps, such as formation of cleaved-edge facets for laser diodes and electrical backside contacts necessary for vertical optical and electrical devices. The extraction of heat from an operating high power device through the sapphire substrate is also hampered. Free-standing GaN substrates, nearly equal in area to the original 2 inch wafer, are produced from 50 to 300 micron thick GaN films grown on sapphire by hydride vapor phase epitaxy. The thick films were separated from the growth substrate by laser-induced liftoff, using the third harmonic from a Q-switched Nd:YAG laser, with 355 nm wavelength and photon energy slightly larger than the GaN band gap, suitable to thermally decompose a thin layer of GaN at the film-substrate interface. Sequentially scanned pulses of 5 ns duration with a 7 mm 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 by mechanical and laser induced wet chemical etching and overgrown by a two micron thick MOCVD GaN layer. By this procedure epi ready free standing substrates are fabricated with low dislocation densities and a surface roughness of about 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 J1.8
THERMOMECHANICAL ANALYSIS OF THE LASER LIFT-OFF PROCESS FOR SEPARATING EPITAXIAL GaN FILMS FROM THEIR SAPPHIRE GROWTH SUBSTRATES. William S. Wong, Alberto Salleo and Tim Sands, University of California, Department of Materials Science and Mineral 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 sapphire 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 sapphire substrate constraint, a new materials integration technique, laser lift-off (LLO), combined with a wafer bonding process has been demonstrated to effectively integrate high-quality GaN grown on sapphire substrates with the superior thermal and electrical conductivity of other substrate materials such as Si. The band-gap selective LLO process involves the localized 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 thermoelastic stress to develop in the film. The calculated spatial 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, 38 ns) pulsed excimer laser showed that a fluence of 400 mJ/cm^2 is needed to raise the GaN surface temperature to the decomposition temperature of ~1000°C. Examination of the GaN surface morphology by scanning electron microscopy for laser fluences between 200-600 mJ/cm^2 confirms the decomposition of the 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 interfacial region. The calculated maximum compressive 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-bonding 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 InGaN blue light-emitting diode membranes have been fabricated using LLO without degradation of the device performance.

11:45 AM J1.9
LASER DAMAGE IN EPITAXIAL Pb(Zr,Ti)O_3 THIN FILMS AND RELATED OXIDES PRODUCED BY EXCIMER LASER LIFTOFF.
L. Tsakalakos 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 liftoff 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 248 nm excimer laser pulse (τ= 38 ns) through the backside of the growth substrate. Therefore, the process presents markedly different thermomechanical boundary conditions compared to conventional laser processing of exposed surfaces. Calculation of the optical absorption length and thermal diffusion length in PZT shows them to be ~25 nm and ~125 nm, respectively. An analytical thermal model of the laser liftoff 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 at ambient (again after 38 ns). Since the equilibrium melting point is ~1280°C for PZT, it is expected that a thin (~100 nm) liquid layer will have formed during application of the laser pulse, as is indeed evidenced by observation of a quenched liquid phase by Scanning Electron Microscopy. However, measurement of the ferroelectric properties after removal of the quenched liquid layer by ion milling show the dielectric constant and loss tangent are reduced after liftoff, from 1135 to 705 and from 0.076 to 0.039, respectively. Materials characterization of the laser damage utilizing 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
Chairs: Kenji Ebihara and Rajiv K. Singh
Tuesday Afternoon, April 25, 2000
Nob Hill C/D (Marriott)

1:30 PM *J2.1
IMAGING AND SPECTROSCOPY OF LASER ABLATED CARBON PLUMES FOR THIN FILM DEPOSITION AND NANOTUBE SYNTHESIS. A.A. Puretzky, Department of Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN; D.B. Geohegan, X. Fan, S.J. Pennycook 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 in efforts to optimize two important application areas: 1. deposition of diamond-like carbon films and 2. carbon nanotube synthesis. 1)Three-component carbon plumes observed during deposition of 'amorphous diamond-like' films in vacuum reveal intraplume 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 photoinduced conversion of the initial ejecta (C_2,C_3)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-catalyst ablation plume were performed to understand how the hot laser

plasma of initial ejecta (containing C, C_2, C_3, and metal catalyst atoms) is influenced by the high-pressure background gas (500 Torr Ar) at the conditions typical for laser ablation synthesis 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 3 s were measured using LIF and laser induced blackbody emission imaging and spectroscopy. The raw soot 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 J2.2
IN-SITU OBSERVATION OF NANOPARTICLE FORMATION AND GROWTH DURING LASER ABLATION. K.S. Seol, Y. Okada, K. Takeuchi, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, JAPAN; R.P. Camata, Institute of Physics, University of São Paulo, São 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-suspended nanoparticles. In this work we have used low-pressure differential mobility analysis to perform high-resolution particle spectrometry in the 1-200 nm size range and study the gas-phase dynamics of nanoparticles formed during 1064-nm pulsed Nd^{3+}:YAG laser ablation of a silicon target in inert gas atmosphere. Background pressures in the 70-400 Torr range and laser fluences between 0.1 and 1.0 J/cm^2 were considered. *In-situ* measurements reveal that the nanoparticle population 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 agglomerates formed by collisions of the small 5-10 nm particles. At low pressures ($<$ 150 Torr) and low laser fluences ($<$ 0.2 J/cm^2), the population is dominated by the 5-10 nm nanoparticles. For a laser fluence of 0.2 J/cm^2, for example, the mean diameter of these small particles changes from 4.5 nm at 70 Torr to 8.5 nm at 300 Torr, while their peak concentration drops from 10^8 to 10^6 cm^{-3} in the same pressure interval. Within the framework of the aerosol general dynamic equation, this pressure dependence suggests particle growth by Brownian coagulation, as the particle size scales with the system residence time. For laser fluences above 0.8 J/cm^2 a surge of particles with sizes around 200 nm is observed. This leads to the depletion of small particles and large agglomerates become the predominant objects in the gas-suspended population.

2:15 PM J2.3
DEPOSITION OF NANOTUBES AND NANOTUBE COMPOSITES USING MATRIX-ASSISTED PULSED LASER DEPOSITION. P.K. Wu, Department of Physics, Southern Oregon Univ., Ashland OR; J. Fitz-Gerald, A. Pique, D.B. Chrisey and R.A. McGill, 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 or suspending the film material in a volatile solvent, freezing the mixture to create a solid target, and using a pulse 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 glycol 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 um diameter dot size. These films can be deposited on 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 SWN, composites of superior quality can be fabricated by MAPLE for protective coatings, electronics, and biomedical applications.

3:00 PM *J2.4
NOVEL NANOCRYSTALLINE METAL AND 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-assembling process. Properties of interfacial regions, which are crucial in mechanical properties of thin film composities, can be controlled by appropriate alloying. Thus, we have fabricated superhard thin film nanocrystalline composities of copper and zinc. We present a model of hardness vs. grain size to explain the mechanical properties over the entire range. A similar approach has been adopted to fabricate semiconductor (Ge, ZnO) nanocrystallines embedded in larger bandgap matrices such as AlN and α-Al_2O_3. 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 J2.5
SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE Nb-ALUMINIDES BY LASER ABLATION TECHNIQUE. Tadashi Yamamoto, Jyoti Mazumder, 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 materials depends strongly on the He backing gas pressure. No nanocrystalline material is 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, determined by transmission electron microscopy (TEM). Crystal structure of the majority of particles is identified as $NbAl_3$ ($D0_{22}$) type. Energy dispersive spectroscopy (EDS) revealed that atomic ratio of Al/Nb decreases from the stoichiometric composition of $NbAl_3$ with increasing laser energy density and decreasing backing gas pressure. High-resolution electron microscopy (HREM) reveals the atomic structure of the $NbAl_3$ particle of the $D0_{22}$ type at all the processing conditions. Nb_3Al particles of the A15-type crystal structure are identified at lower gas pressure and higher laser energy. X-ray diffraction reveals that particles of small- and large- modes are synthesized at the same time and the volume ratio of the two distributions is between 0.7 and 1.1. Formation mechanisms of the nanocrystalline powders is proposed in view of the structure-processing relationships.

3:45 PM J2.6
SYNTHESIS AND CHARACTERIZATION OF INDIUM NITRIDE PARTICLES THROUGH REACTIVE LASER ABLATION. Amith Murali, Valerie Leppert, Ian Kennedy, Subhash Risbud, 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 (99.9999%) target in flowing high purity nitrogen atmosphere. The nitrogen pressure was maintained at $\sim$100 Torr throughout the synthesis with a flow rate of about 0.6 l/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 $\sim$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 J2.7
OPTICAL AND STRUCTURAL CHARACTERISTICS OF GOLD NANOCRYSTALLITES EMBEDDED IN A DIELECTRIC MATRIX. A.K. Sharma, A. Kvit, 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 metal particles 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 at a desired location in the host lattice. By changing the thickness or the particle size of the metals, the collective excitation frequency or surface plasmon frequency of the metal can be varied1 and thus, the optical absorption frequency can be altered. We have fabricated a novel multilayer structure comprising alternate layers of gold nanoparticles and amorphous alumina on c-plane sapphire and Si (100) substrates. Pulsed laser deposition was employed to fabricate these size-selective multilayer composites. The characterization of these specimens was performed using high resolution transmission electron microscopy (HRTEM), ellipsometry, optical transmission and absorption measurements and nanohardness measurements. The optical absorption in the visible range has been observed in these composite films which is believed to originate from the surface plasmon resonances of the gold clusters. The results point out the success of PLD in tailoring the optical and mechanical properties of these composites with thickness and size.

4:15 PM J2.8
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. Kohn, MPI fuer Stroemungsforshung, Goetingen, GERMANY; R. Alexandrescu, S. Cojocaru, A. Crunteanu, 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 produced via laser pyrolysis of iron pentacarbonyl in a flow reactor. Using the sensitizer C_2H_4, a CW CO_2 laser with a power of 70 Watt was employed. The samples have been carefully passivated before exposing them to air. Selected area electron diffraction (SAED) studies revealed the presence of α-Fe, with important contributions from magnetite (Fe_3O_4) and hematite (α - Fe_2O_3). The 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 toluene extraction and IR transmission spectroscopy. A comparison with previous reported results on iron carbine-based nanopowders, synthesized at higher laser power (~130 Watt) is also presented.

4:30 PM J2.9
NOVEL ZINC NANOCRYSTALLINE COMPOSITES BY PULSED LASER DEPOSITION. Ravi K. Venkatesan, A.K. Sharma, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have developed a novel processing technique to fabricate artifact 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 nanocrystalline composites. The grain size of zinc 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 insoluble in zinc. Using this approach, we have fabricated nano-composites of grain sizes ranging from 10 nm to 100 nm. The potential is to go even lower. The hardness increases with the decrease in grain size, following approximately Hall-Petch relationship. The role of W in grain boundary deformation is of particular interest in strengthening the nanocrystalline composites.

SESSION J3: POSTER SESSION: LASER-SOLID INTERACTIONS FOR MATERIALS PROCESSING

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

J3.1
PLASMA AND DLC FILM CHARACTERISTICS FROM PULSED LASER ABLATION OF SINGLE CRYSTAL GRAPHITE AND AMORPHOUS CARBON: A COMPARATIVE STUDY EMPLOYING 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 ion kinetic energy, plume profile, C_2 formation mechanism, and complex molecule concentration. Plume electron density is found to be ~ 10–12 % lower near the target in SCG than a-C plumes consistent with mass loss inventory measurements, whereas ion fractions are estimated in the range ~ 10–15 % for both target cases. Plume 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 target. For both target cases, we find T_e drop off with position away 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 plasma 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 C_2 at high fill pressures [R. M. Mayo, *et al*, J. Appl. Phys., **86**, 2865 (1999)]. A significantly smaller profile peaking factor for SCG plumes supports this conclusion. Less energetic and slightly lower temperature SCG plume conditions are consistent with reduced peaking and more massive plume species. Plasma plumes from SCG targets exhibit laser energy (E_l) dependent peaking, again consistent with more complex molecules increasingly disassociated with E_l increase. The E_l dependence further suggests the potential for control of particle size distribution and plume profile peaking, though not independently. 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 liberates about twice the number of ^{12}C atoms from the target per unit E_l. In addition, high pressure background fill indicates lesser plume energy attenuation for SCG plumes, again suggesting the presence of more massive particles.

J3.2
IMPROVEMENT OF CAVITATION EROSION RESISTANCE AND CORROSION RESISTANCE OF BRASS BY LASER SURFACE MODIFICATION K.F. Tam, F.T. Cheng, The Hong Kong Polytechnic Univ, Dept of Applied Physics, Hong Kong, PR CHINA; H.C. Man, The Hong Kong Polytechnic Univ, Dept of Manufacturing Engineering, Hong Kong, PR CHINA.

Laser surface modification of brass (Cu-38Zn-1.5Pb) using AlSiFe and NiCrSiB alloy was achieved by using a 2kW continuous wave Nd-YAG laser with the aim of improving the cavitation erosion resistance and corrosion resistance. The alloying powder was preplaced on the brass substrate by thermal spraying to a thickness of 150-300 μm, 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 anodic polarization characteristics of the laser surface modified specimens in 3.5% 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 potentiostat respectively. The cavitation erosion resistance of the specimens modified with AlSiFe 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 AlSiFe deteriorated, as reflected 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 microstructure and the surface morphological of the specimens were investigated with the aid of SEM and optical microscopy.

J3.3
ABLATION-INDUCED STRESSES IN FUSED SILICA BY 157-NM F_2-LASER IRRADIATION. Igor A. Konovalov and Peter R. Herman, University of Toronto, Department of Electrical and Computer Engineering, Toronto, ON, CANADA.

The F_2 laser is a promising source for direct etching of micro-structures and the precise shaping of optical-grade surfaces on wide bandgap materials such as fused silica [1]. The threshold fluence for material removal is high in glass (>1 J/cm^2), and radiation exposures to the underlying bulk glass can therefore reach moderately high laser doses (~100's J/cm^2) with only several 'micomachining' 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. This bending-plate method provided a measure of the strain and showed that residual stresses were tensile at the ablated surface. By thinning the sample with chemical etching, the thickness and profile of the laser-induced stresses was 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 long exposures at sub-ablation fluence were applied. Possible mechanisms for these changes and their relation to material stresses will be discussed.
[1] P.R. Herman, A. Oettl, K.P. Chen, and R.S Marjoribanks, SPIE Proc. 3616, 1999, pp. 148-155.

J3.4
LASER INDUCED FLUORESCENCE MEASUREMENT OF PLASMA PLUME DURING PULSED LASER DEPOSITION OF DIAMOND-LIKE CARBON. Yukihiko Yamagata, Yuji Kozai, Fumiaki Mitsugi, Tomoaki Ikegami, Kenji Ebihara, Kumamoto Univ, Dept of Electrical and Computer Engineering, Kumamoto, JAPAN; Ajay Sharma, Jagdish Narayan, 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 sp^3 formation exceeding 80%. However, the detailed mechanism of the PLD process to prepare the DLC film has not 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 one of 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 irradiate an amorphous carbon target with an incident angle of 45 degree. A dye laser (Lambda Physik, Scanmate 2) beam was tuned at 516.52 nm to excite C_2 molecules ((0,0) $a^3\Pi_u$ - $d^3\Pi_g$), and introduced into the ablation plume along with parallel to the target surface. A delay pulser changed the delay time of the probing laser after the KrF laser irradiation. Laser induced fluorescence of 563.49 nm ((0,1) $d^3\Pi_g$ - $a^3\Pi_u$) was successfully detected at a right angle of both laser beams by a monochromator equipped with a photomultiplier tube. Strong LIF was observed at a distance of 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 first 200 ns. It suggests that C_2 molecules are formed near the target as a result of recombination of carbon atoms and/or dissociation of heavier particles.

J3.5
STRUCTURAL CHARACTERIZATION OF LASER LIFT-OFF GaN. E.A. Stach and M. Kelsch, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; W.S. Wong, N. Chung and T. Sands, 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 disimilar 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 sapphire substrate. This yields a free standing 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 electron microscopy and diffraction contrast microscopy indicate that the interface between the HVPE GaN and the sapphire substrate before lift-off is highly strained and defective (as would be anticipated from the 14.2% lattice mismatch between these two materials) and that there are semi-periodic 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 Al_2O_3 layers following lift-off shows that the laser deteriorates 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 increases the structural perfection of the layer. 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 interfaces. 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 FOM HIGHLY IONIZED DUAL-LASER GENERATED PLASMAS. Alfred M. Miyawa, Sarath Witanachchi and Pritish 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 plume. Ionization yields in excess of 60%, in comparison with 4-10% in single laser ablation, are possible with dual-laser ablation. The spatially overlapped and temporally synchronized excimer and CO_2 laser pulse combination produces 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 sp^3 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 spectroscopic techniques to study the enhancement in ionization and spatial ion distribution in dual-laser ablated carbon plumes. 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 deconvolved to yield two peaks, one characterizing the sp^3 bonding (D-band) around 1350 cm^{-1} and the other representing the sp^2 (G-band) around 1550 cm^{-1}. The ratios of intensities corresponding to these peaks have been used to gauge the relative sp^3 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. DMI-9622114) and the US Department of Energy (Grant No. DE-FG02-96ER12199).

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

Thin amorphous films of tantalum oxide (TaO_x)J films were grown on borosilicate glass (BK7) substrates by KrF (248 nm) excimer pulsed laser ablation of a Ta_2O_5 target, in an oxygen environment. The substrates wore heated during deposition to a temperature of 250 or 400°C, while tire oxygen pressure was set in the range 5 to 30 mTorr. The films were found to be stoichiometric Ta_2O_5 for O_2 pressures above 10 mTorr. The refractive index and extinction coefficient of the TaO_x films were simultaneously measured by spectral reflectance and transmittance, with wavelengths in the range 250 to 850 nm and 420 to 1000 nm, respectively. For all growth conditions, best fitting on the reflectance and transmission curves was achieved by assuming two layers on top of the BK7 substrate. For λ = 633 nm, refractive indices between 2 and 2.3 were obtained for both layers, along with extinction coefficients of $5x10^{-2}$ to less than 10^{-4}, depending on the processing parameters. High-resolution cross-sectional electron microscopy was used to investigate the vicinity of the TaO_x/BK7 interface.

J3.8
INVESTIGATION ON LASER-INDUCED EFFECTS IN NANOSTRUCTURE FABRICATION WITH LASER-IRRADIATED SCANNING TUNNELING MICROSCOPE TIPS IN AIR AMBIENT. Z.H. Mai, Y.F. Lu, W.D. Song and W.K. Chim, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, SINGAPORE.

Nanostructure fabrication using lasers in combination with a scanning microscope (STM) has been reported in the past several years. Different mechanisms have been proposed for the formation of 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 in the mechanism of nanostructure fabrication, a detail investigation is necessary. In this paper, we report our investigation on the kinetics of nanostructure fabrication on gold films and 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 sufaces is more than 27 nm. The thermal expansion length of the tip under 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 indention is the primary reason of nanostructure formation, while for H-passivated Ge surfaces, optical enhancement is the only reason.

J3.9
MAGNETIC FIELD GENERATION AT EARLY STAGE OF KrF EXCIMER LASER ABLATION OF SOLID SUBSTRATES. M.H. Hong, Y.F. Lu and A. Foong, Laser Microprocessing Laboratory, Dept of Electrical Engineering and Data Storage Institute, National Univ. of Singapore, SINGAPORE.

Magnetic field generation at early stage of KrF 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-turn coil is applied to detect signals induced by 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 as a double peak distribution with the negative peak appearing first. The peak duration is around 30 ns. As 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 on 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.

J3.10
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 film with in-situ heating exhibits a preferential c-axis orientation normal to the film plane and has large perpendicular magnetic anisotropy. The grains in the film have good crystallinity with hexagonal symmetry. The perpendicular and in-plane coercivities are 2.8 and 1.5 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 one are all 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 to the film deposited with in-situ heating.

J3.11
STUDY OF TETRAHEDRAL AMORPHOUS CARBON WITH DIAMOND INCLUSIONS SYNTHESIZED BY HYPERTHERMAL CARBON SPECIES. J.P. Zhao and Z.Y. Chen, Shikoku National Industrial Research Institute, Takamatsu, JAPAN and ION Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, CHINA; T. Yano, T. Ooie and M. Yoneda, Shikoku National Industrial Research Institute, Takamatsu, JAPAN.

Tetrahedral amorphous carbon (ta-C) films have been synthesized by two hyperthermal processes: pulsed laser ablation (PLA) and filtered arc deposition (FAD). In the case of PLA, laser fluence had remarkably effect on the structure and properties of ta-C. Particle density and size reduced with decreasing fluence; however, film density and optical properties were optimized at moderate fluence. The maximum density ($\sim$3.0 g/cm^3) and sp^3 content ($\sim$80%) were obtained at fluence of 6.5 J/cm^2. Transmittance, optical bandgap, and UV absorption edge were also reach to extreme values at this fluence. By calculating film thickness from interference of reflection spectrum, we found that the minimum interval between calculated and measured thickness could be achieved by introducing refractive index, n(λ), of diamond into calculation process for 6.5 J/cm^2 deposited ta-C. For higher or lower fluence, film quality degraded obviously; density and optical bandgap decreased toward those of common amorphous carbon (a-C), and the thickness calculation had to introduce n(λ) of IBAD a-C. Micro-Raman analyses indicated that higher or lower fluence led ta-C to resemble a-C; however, additional Raman bands around 1168 cm^{-1} and 1271 cm^{-1} were observed in film deposited at moderate fluence, which could be assigned as nanocrystalline or hexagonal diamond inclusions according to phonon density of states (DOS) calculation. Moreover, benzene-like structure was also observed in micro-Raman analyses. On the other hand, more tetrahedrally bonded films ($\sim$90% sp^3 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 ta-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 ta-C.

J3.12
PULSED ELECTRON BEAM ABLATION OF $CuInSe_2$ - COMPARISON WITH PULSED LASER ABLATION. Serghei Malkov, Ctr 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 $CuInSe_2$ (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 plume diagnostic studies has been performed in [1] where it is established an existence of less quantity 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 pulsed electron beam ablation the CIS deposition was implemented by a pulsed plasma induced high current and magnetically self pinched electron beam produced in a low pressure channel spark camera at the following operation conditions: high voltage -10 - 20 kV, pulse duration - 100 ns, repetition rate - 1 - 5 Hz, power density <500 MW/cm^2, argon pressure - 1 - 3 Pa, substrate temperatures - 250 - 550C. The CIS thin films are found to have a strong preferential (112) orientation, the chalcopyrite structure, columnar grain microstructure. The Cu/In ratio in the films was obtained to be temperature dependent and in a range of 0.9 - 1.2. A well-defined absorption edge near the band gap with an energy gap of Eg=0.99 eV has been observed for the CIS films. Moreover, the results of post deposition annealing of the low substrate temperature CIS films by means of the pulsed electron beam under different beam parameters are presented.
1. S.D. Kovaleski, R.M. Gilgenbach, L.K. Ang, Y.Y. Lau, J.S. Lash, Applied Surface Science 127-129 (1998) 947.

J3.13
EPITAXIAL ZnO FILMS GROWN BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION. V. Craciun, N.D. Bassim, R.K. 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. Craciun, Laser Department, National Institute for Laser, Plasma, and Radiation Physics, Bucharest, ROMANIA.

ZnO is an interesting semiconductor material that has been used for transparent and conductive films, varistors and chemical sensors. It also exhibits nonlinear optical and piezoelectric properties and has been used as a light modulator, a planar 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 (UVPLD) technique where an ultraviolet source was added to the deposition chamber. The UV source is irradiating the film during the laser ablation-growth process 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, as assessed by Rutherford backscattering, transmission 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 PLD. The optical, electrical, and microstructural characteristics of these 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.

J3.14
ROLE OF OXYGEN CONTENT AND CRYSTALLINITY IN MAGNETORESISTANCE BEHAVIOR OF LANTHANUM MANGANITE THIN FILMS. S.V. Pietambaram*, D. Kumar*, Rajiv K. Singh*, C.B. Lee**. *Department of Materials Science and Engineering, University of Florida, Gainesville, FL, **Department of Electrical Engineering, North Carolina A&T University, Greensboro, NC.

Although colossal magnetoresistance in lanthanum calcium manganite (LCMO) thin films is known since a long time, the effect of oxygen content and crystallinity on the properties of these films is not 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 heat treatments. A series of LCMO thin films have been grown in situ on (100) $LaAlO_3$ substrates using a pulsed laser deposition technique under identical conditions. These films were subjected to the following post-deposition heat treatments: 500°C oxygen anneal for 12 hours, 500°C Ar anneal for 12 hours, 900°C oxygen anneal for 2 hours, 900°C Ar anneal for 2 hours, 900°C oxygen anneal and quenched to room temperature and 500°C vacuum annealing for 1 hour. As deposited LCMO films show a transition temperature of 120 K and an MR ratio (defined as [R(0)-R(H)/R(H)], where R(0) and R(H) are resistance in zero and applied magnetic fields) of 104%. The samples subjected to a 500°C oxygen, Ar and vacuum annealing have shown deteriorated magnetoresistance properties. The films subjected to 900°C annealing in Ar and oxygen ambient have shown a significant improvement in the metal-to-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 manganite thin films.

J3.15
EPITAXIAL GROWTH OF β-C_3N_4 ON A NITRIDATED DIAMOND SURFACE BY NITROGEN-ARC-DISCHARGE-ASSISTED LASER ABLATION DEPOSITION. Pei-Nan Wang, Ning Xu, Xuan-Tong Ying, Zhi-Feng Ying, Zheng-Ping Liu and Wei-Dong Yang, Fudan Univ, State Key Joint Lab for Materials Modification by Triple Beams, Dept of Physics, Shanghai, CHINA.

A diamond film was nitridated by low-energy nitrogen ion implantation. The nitrogen ion source was a home-made device using glow discharge to generate nitrogen ion beams. The mass spectrum shows that the ratio of N^+/N_2^+ is as high as 5/1. The Raman spectrum shows that the β-C_3N_4 phase was formed in the diamond surface after nitrogen implantation. Epitaxial growth of β-C_3N_4 was carried out on this nitridated diamond film by nitrogen-arc-discharge-assisted laser ablation deposition. A high-purity graphite rod was ablated by a frequency doubled Nd:YAG laser. A pure nitrogen gas flow was passed through a magnetically confined, arc-heated 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 were characterized by Raman and infrared (IR) spectroscopy. There were eight narrow Raman peaks observed in the range of 150-1550 cm^{-1}. Seven of them match well with the calculated Raman frequencies of β-C_3N_4, revealing the formation of the β-C_3N_4 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 absorption spectrum of the film shows two peaks at 1444 and 1620 cm^{-1}, which also match with the calculated ones of β-C_3N_4.

J3.16
FUNCTIONALLY GRADIENT DIAMONDLIKE FILMS. R.J. Narayan, Wake Forest Univ, School of Medicine, Winston-Salem, NC; Q. Wei, A.K. Sharma, J. Narayan, North Carolina State Univ, 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 with SP^3 fraction exceeding 80%. However, these films peal off due to high internal compressive stresses. These stresses can 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 enhanced antimicrobial properties. The details of this as well as role of dopants on SP^3 fraction of DLC films will be presented.

J3.17
RAMAN STUDIES OF $LiMn_2O_4$ FILMS GROWN BY LASER ABLATION. M.A. Camacho-Lopez, C. Julien, LMDH, Universite Pierre et Marie Curie, Paris Cedex, FRANCE; L. Escobar-Alarcon, E. Haro-Poniatowski, Universidad Autonoma Metropolitana Iztapalapa, Laboratorio de Optica Cuantica, Mexico DF, MEXICO.

$LiMn_2O_4$ films were grown onto Si substrates heated at temperature lower than 300°C using the pulsed-laser deposition (PLD) from a sintered composite target ($LiMn_2O_4$+Li_2O) irradiated with a Nd:YAG laser. The structural characterizations of these films have been carried out by Raman scattering (RS) spectroscopy which probe the local environment of cations in the $LiMn_2O_4$ framework. RS spectra of PLD $LiMn_2O_4$ films have been investigated as 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 (Fd3m space group). Information for the structural quality of the PLD $LiMn_2O_4$ 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 Li_2O*10%, the RS spectra are less resolved and the stretching Mn-O peak is broadened toward the high wavenumber side due to the high distortion of MnO_6 octahedra. These spectroscopic results indicate that the conjonction of target composition (lithium-rich), substrate temperature (Ts=300°C), and partial oxygen pressure ($P(O_2)$=100 mTorr) promotes reconstruction of the stoichiometric $LiMn_2O_4$ spinel framework.

J3.18
SURFACE MORPHOLOGY OF PZT THIN FILMS PREPARED BY PULSED LASER DEPOSITION. Masaaki Yamazato, Masamitsu Nagano, Saga Univ, Dept of Chemistry and Applied Chemistry, Saga, JAPAN; Kenji Ebihara, Kumamoto Univ, Dept of Electrical and Computer Engineering, Kumamoto, JAPAN.

Pulsed laser deposition (PLD) has been used successfully in synthesizing many kinds of films, because PLD is very attractive process, especially, for oxide thin 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 assist film growth and to promote surface solid state reactions. In this paper, $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin films have been grown on MgO substrate using a pulsed KrF excimer laser deposition system. The films were deposited under the wide oxygen pressure range 0.1 - 5 Torr at substrate temperature of 550°C and laser fluence of 2 J/cm^2. 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 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; $d_m \propto p^{0.37}$, where d_m and p indicate diameter of PZT particle and oxygen gas pressure, respectively.

J3.19
SYNTHESIS OF CUBIC $Zn_xMg_{1-x}O$ SINGLE CRYSTAL FILMS BY PULSED LASER ABLATION. A.K. Sharma, C. Jin, A. Kvit, 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; O.W. Holland, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

We have synthesized epitaxial cubic $Zn_xMg_{1-x}O$ thin films with x upto 0.2 on MgO (100) substrates using pulsed laser deposition. In this composition range, ZnMgO phase is cubic with lattice constant of the film (a_f=4.22 Å) matching very closely with that of the substrate (a_s=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 3-D epitaxial hetero-structures of ZnMgO/TiN/Si (100) layers. The characterization of layers was accomplished by X-ray diffraction, high resolution transmission electron microscopy (HRTEM), Rutherford back-scattering spectroscopy/ion channeling (RBS), and optical measurements. HRTEM results have brought out single crystal nature of the films and have revealed details of the microstructure such as

defects. The ion chanelling yield as low as 3% was achieved in the epitaxial films indicating a good quality of the crystal. Optical results have also been discussed in this work. These composite 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-STRUCTURES OBTAINED BY LASER-ASSISTED CVD METHODS. R. Alexandrescu, A. Crunteanu, C.S. Cojocaru, R. Cireasa, I. Voicu, I. Morjan, National Institute for Lasers, Plasma and Radiation Physics, Bucharest, ROMANIA; Marlène Charbonnier, Maurice Romand, LSIS, Université Claude Bernard - Lyon 1, Villeurbanne Cedex, FRANCE.

Iron-based compounds have a large number of applications in modern technologies due to their structural, magnetic and catalytic properties. The aim of this paper is to present the production of iron and iron carbide thin films and nanostructures by IR laser-stimulated processes in gas mixtures containing iron pentacarbonyl (vapor). In case of iron carbide film synthesis, a suitable hydrocarbon precursor (C_2H_2) was added to the sensitized precursor mixtures. By using different analytical methods (XPS, IR spectrophotometry, electron microscopy) the influence of the experimental conditions on the composition and structure of the as-deposited films will be discussed.

J3.21
LOW TEMPERATURE GROWTH OF BARIUM STRONTIUM TITANATE FILMS BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION. V. Craciun, J.M. Howard, A. Srivastava, N.D. Bassim and R.K. 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.

The properties of $Ba_{1-x}Sr_xTiO_3$ thin layers grown on (100) Si and corning glass substrates using an in-situ ultraviolet (UV)-assisted pulsed laser deposition (UVPLD) technique have been studied. An excimer laser (KrF, 248 nm) emitting 25 ns long pulses was used for ablation. A vacuum compatible, low pressure Hg lamp capable of dissociating molecular oxygen into ozone and atomic oxygen, was fitted into the PLD system. It allows for in-situ UV irradiation during both the laser ablation-growth process and the cooling stage, exposing each deposited layer to the action of more reactive gaseous species formed by UV photodissociation. The crystalline structure of the grown layers was investigated by x-ray diffraction (XRD) and transmission electron microscopy (TEM), while the chemical composition and bonding were investigated by x-ray photoelectron spectroscopy (XPS). The optical properties of films grown on Si substrate were investigated by spectroscopic ellipsometry and those of films grown on corning glass by spectrophotometry. These investigations showed that, with respect to conventional PLD grown films under similar conditions but without UV illumination, UVPLD grown films exhibited better crystallinity, especially for films grown at lower substrate temperatures. These films also possess higher dielectric constant values, reduced leakage currents, contained less physisorbed oxygen, and exhibited a better overall stoichiometry. The UVPLD technique was especially effective at moderate processing temperatures, where the thermal energy available for the growth process is comparatively low.

J3.22
TANTALUM NITRIDE THIN FILMS SYNTHESIZED BY PULSED Nd:YAG LASER DEPOSITION METHOD. Hiroharu Kawasaki, Kazuya Doi, Satoshi Hiraishi and Yoshiaki Suda, Department of Electrical Engineering, Sasebo National College of Technology, Sasebo, Nagasaki, JAPAN.

Tantalum nitride (TaN) films have been deposited on silicon (100) substrates by using a pulsed Nd:YAG laser deposition method. Surface morphology and structure of the films have been obtained by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) measurement. These results suggest the substrate temperature (Ts) is one of the most important parameters to prepare crystalline TaN thin films. XRD pattern shows that all as-deposited films are almost amorphous at Ts $\leq$ 300 °C, and crystalline TaN films are obtained at Ts $\geq$ 500 °C. Grain sizes of the films, examined with a SEM, increase with increasing Ts.

J3.23
PROPERTIES OF THE MAGNETORESISTIVE $La_{0.8}Sr_{0.2}MnO_3$ FILM AND INTEGRATION WITH $PbZr_{0.52}Ti_{0.48}O_3$ FERROELECTRICS. Fumiaki Mitsugi, Tomoaki Ikegami, Kenji Ebihara, Kumamoto Univ, Dept of Electrical and Computer Engineering, Kumamoto, JAPAN; J. Narayan, North Carolina State Univ, Dept of Materials Science and Engineering, North Carolina State University; A.M. Grishin, Royal Institute of Technology, Dept of Condensed Matter Physics, Stockholm, SWEDEN.

The magnetoresistive $La_{0.8}Sr_{0.2}MnO_3$(LSMO) film and ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$(PZT)/LSMO heterostructures were prepared on the MgO (100) single crystal substrates by KrF excimer pulsed laser deposition (PLD) technique. The LSMO film deposited at 850°C, $O_2$100mTorr and laser energy density of 2J/cm^2 (5Hz) has a resistivity peak temperature of 295K. The X-ray diffraction pattern showed (00l) c-axis orientation. The Atomic Force Microscopy image showed very smooth surface morphology (maximum roughness < 10nm) with the mean grain size of about 100nm. 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 Au/PZT/LSMO/MgO capacitor indicated remanent polarization of 22μC/cm^2 and coercive field of 50kV/cm (applied voltage 10V, 1kHz).

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

NOTE EARLY START

8:15 AM J4.1/V5.1
AN IMPROVED METHOD OF UV LASER DIRECT-WRITE DEPOSITION OF MATERIALS FOR MICROELECTRONICS APPLICATIONS. K.M.A. Rahman, D.N. Wells and M.T. Duignan, Potomac Photonics, Inc., Lanham, MD.

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

8:30 AM *J4.2/V5.2
LASER GUIDED DIRECT WRITING OF ELECTRONIC COMPONENTS. Michael J. Renn, Marcelino Essien, Bruce H. King and W. Doyle Miller, Optomec Design Company, Albuquerque, NM.

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

9:00 AM J4.3/V5.3
LASER INDUCED ETCHING OF Si WITH NF3 USING CuBr LASER. B. Ivanov[1], M.P. Tarassov[2], L. Zambov[1]. [1]Dept. of

Semiconductors, University of Chemical Technology and Metallurgy, Sofia, BULGARIA, [2]Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Science, Sofia, BULGARIA.

Laser induced etching of Si with NF3 were investigated using the focused beam of copper bromide vapor laser with wavelengths of 510 and 578 nm in vacuum system. The laser average power was in the range 4-10 W with repetition rate - 20 kHz and the pulse duration - 60 ns. NF3 was used at partial pressure in the range 1 - 1000 mbar. The basic process parameters were varied in the ranges: scanning speed from 5 to 400 (μm/s) and substrate temperature of 100 and 400°C, respectively. The etched structures were investigated by Scanning Electron Microscopy (SEM). The influence of the process parameters - laser power, scanning speed, NF3 pressure and background temperature of the width and depth of etched groves was studied. The etched rates 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 (VUV) and ultraviolet (UV) radiation generated by novel excimer sources are discussed. Compared with conventional sources, these excimer lamps offer narrow-band radiation at various wavelengths from 108 - 354nm and over large areas. Since excimer complexes have no stable ground states self-absorption of the emitted radiation in the discharge is avoided. As a consequence, high efficiencies at high power densities can be achieved. The variety of available wavelengths offers an enormous potential for new industrial applications in materials processing. Previously, photo-oxidation of silicon, germanium and silicon germanium and photo-deposition of single- and multi-layered films of silicon oxide, silicon nitride, and silicon oxynitride have been demonstrated. In this paper, UV-induced growth of high dielectric constant (tantalum oxide, titania, or PZT) and low dielectric constant (polyimide and porous silica) thin films by photo-CVD and sol-gel processing, as well as the effect of low temperature UV annealing, are discussed. Film properties, determined using ellipsometry, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV spectrophotometry, scanning electron microscopy (SEM), and electrical characterisation, showed that good quality layers could be produced. Leakage current densities as low as 0.9 pA/sq.cm and 32μA/sq.cm have been obtained for the as-grown tantalum oxide films formed by photo-induced processing and photo-CVD, respectively - several orders of magnitude lower than for other as-grown films prepared by any other technique. A subsequent low temperature (400°C) UV annealing step improves these to 2nA/sq.cm at 0.5 MV/cm and 7nA/sqcm, respectively. These values are essentially identical to those only previously obtained for films deposited by alternative methods and annealed at temperatures between 600 and 1000°C. The applications investigated so far clearly demonstrate that low cost high power excimer lamp systems can provide an interesting alternative to conventional UV lamps and excimer lasers for industrial large-scale low temperature materials processing.

9:45 AM J4.5/V5.5
LASER DIRECT WRITE OF CONDUCTING AND INSULATING TRACKS IN SILICON CARBIDE. Deepak Sengupta and Aravinda Kar, Laser-Aided Manufacturing, Materials and Micro-Processing Laboratory, School of Optics and Center for Research and Education in Optics & Lasers (CREOL), The University of Central Florida, Orlando, FL; Nathaniel R. Quick, Applicote Associates, Lake Mary, FL.

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

10:15 AM J4.6/V5.6
LASER GUIDED DIRECT WRITING. Robert Pastel, Peter Geiser, Edward Nadgorny, Dept of Physics; Allan Struthers, Math. Sci. Dept, Michigan Technological University, Houghton, MI.

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

10:30 AM J4.7/V5.7
CFD MODELING OF LASER GUIDED PARTICLE DEPOSITION FOR DIRECT-WRITE FABRICATION. J.C. Sheu and M.G. Giridharan, CFD Research Corp., Huntsville, AL.

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

10:45 AM *J4.8/V5.8
NOVEL METHOD FOR LASER DIRECT WRITING MESOSCOPIC CONFORMAL ELECTRONIC DEVICES AND SENSORS. James M. Fitz-Gerald, A. Piqué, R.C.Y. Auyeung, H.D. Wu, S. Lakeou, D.B. Chrisey, Naval Research Laboratory, Washington, DC.

Attention to the field of non-lithographic processing has increased in recent years in response to a need to develop a rapid prototyping technique that is capable of rapidly fabricating integrated electronic devices and sensors, ranging in size from 5 -200 microns. We present a novel method to direct write materials onto planar and non-planar substrates at room temperature and under atmospheric pressure. The process utilizes using a pulsed laser to transfer material from a donor ribbon onto an acceptor substrate with a feature resolution of 5 microns. The donor ribbon consists of a 2 quartz wafer with a single side coated with a powder and/or a metal organic precursor of interest (metals, ferrites, ferroelectrics, etc.). The transfer efficiency and resolution have been determined as a function of the ribbon manufacture properties, laser fluence, material properties, and the transfer distance between the donor ribbon and the acceptor substrate. Donor ribbons were manufactured with metal organic precursors alone and in combination with powders to further enhance substrate adhesion and bulk density properties. A pulsed excimer laser (λ = 248 nm) was focused down to average spot sizes ranging from 10 - 100 microns with fluences ranging from 0.5 to 2 J/cm^2 at repetition rates between 1-20 Hz. Glass, alumina, duroid and silicon ranging in thickness from 75 microns - 1 mm were used as substrates. Metallic and complex oxide materials were transferred in single and multi-layer fashion to form capacitors, resistors, conductors, and inductors on the mesoscopic scale successfully. In-situ and ex-situ annealing of the

transferred materials was performed by both pulsed ND: YAG laser (l= 1.06 microns) and conventional furnace heat treatments at 250°C to increase the substrate adhesion and to transform the metal organic while removing the organic precursor material. Chemical composition analysis was performed by X-ray diffraction. Morphological characterization was performed by scanning electron microscopy and 3-D surface profilometry. Electrical characterization was performed with a HP 4291B Impedance Analyzer.

11:15 AM J4.9/V5.9
LASER PROCESSING OF PARMOD FUNCTIONAL ELECTRONIC MATERIALS. Paul H. Kydd, David L. Richard, Parelec, Inc. Rocky Hill, NJ; Kenneth H. Church, CMS Technetronics, Stillwater, OK; Douglas B. Chrisey, Naval Research Laboratory, Washington, DC.

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

11:30 AM J4.10/V5.10
NUMERICAL SIMULATION OF LASER INDUCED SUBSTRATE HEATING FOR DIRECT WRITE OF MESOSCOPIC INTEGRATED CONFORMAL ELECTRONICS (MICE).
Sam Lowry, Sandip Mazumder, J.C. Sheu, CFDRC, Huntsville, AL; Robert Stewart, CMS Technetronics Inc., Stillwater, OK.

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

11:45 AM J4.11/V5.11
THERMAL STABILITY AND ANALYSIS OF LASER DEPOSITED PLATINUM FILMS. G.J. Berry, J.A. Cairns, M.R. Davidson, Y.C. Fan, A.G. Fitzgerald, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee, UNITED KINGDOM; A.H. Fzea, J. Lobban, P. McGivern, J. Thomson, Department of Chemistry, University of Dundee, Dundee, UNITED KINGDOM; W. Shaikh, Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UNITED KINGDOM.

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

SESSION J5: LASERS IN MICROMACHINING AND SURFACE MODIFICATION
Chairs: David P. Norton and Jay Narayan
Wednesday Afternoon, April 26, 2000
Nob Hill C/D (Marriott)

1:30 PM *J5.1
LASER-SOLID INTERACTIONS FOR MATERIALS PROCESSING.
Chris B. Schaffer, André Brodeur, José F. García and Eric Mazur, Harvard University, Department of Physics and Division of Engineering and Applied Sciences, Cambridge, MA.

By focusing femtosecond laser pulses with high numerical-aperture microscope objectives, we micromachine optical glass using energies that are in the range of unamplified 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 absorption through nonlinear 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 microstructuring 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 bandgap of the material, and the energy of the laser pulse. The potential of our technique for producing technologically-relevant structures such as waveguides and Bragg gratings, as well as the advantages of micromachining with only an oscillator instead of a complicated, expensive amplifier chain, will be discussed.

2:00 PM J5.2
MICROSTRUCTURING OF POLYMERS USING LIGHT-CONTROLLED MOLECULAR MOTORS. Celine Fiorini, Christine Denis, Paul Raimond, Jean-Michel Nunzi, 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. Azo-dye aromatic 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 molecules rotation within the matrix leading finally to a full reorientation of the dye molecules. Actually, such phenomenon was applied to all-optical polar ordering. More recent results on photoinduced surface-relief gratings have also opened the way to mass-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 grating could also be simultaneously evidenced optically. Such result indicates that surface-relief grating formation obviously follows chromophores migration from high intensity to low intensity regions, photoinduced molecular movements leading to polymer chain migration. We propose a simple model based on photoinduced azo-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 J5.3
PROCESS MODELING OF THE LASER INDUCED SURFACE MODIFICATION OF CERAMIC SUBSTRATES FOR THERMAL AND ELECTRICAL LINES IN MICROSYSTEMS. Herbert Gruhn, Roland Heidinger, Magnus Rohde, Sabine Rüdiger, Forschungszentrum Karlsruhe, Institute for Material Research I, Karlsruhe, GERMANY; Johannes Schneider, Karl-Heinz Zum Gahr, Universität Karlsruhe, Institute of Materials Science and Engineering II, Karlsruhe, GERMANY.

For many applications in microsystems technology the question of thermal and electrical management 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 laser induced surface modification. The advantages are free design and a good bonding to the substrate. By adding particles with 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 precoating process.

Due to a minimal feedable particle size homogeneous conducting paths generated by the injection process are limited down to a line width of 0.8 mm. For the precoating process a smaller particle size can be used. Therefore line widths of 0.4 mm are reached. To achieve this improvement a special vacuum furnace was developed to avoid the oxidation of the metallic precoating during substrate preheating which is necessary to prevent thermal cracking. Further work has the aim to reduce the line width down to 0.2 mm. 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 set-up to support 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. Bath convection is most responsible for the form of the 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 and velocity. On the other side this assumption can not describe satisfactory bath convection in Cordierite. Therefore a new model will be developed using the fluid dynamic program FIDAP.

3:00 PM *J5.4
VUV EXCIMER LASER ABLATION OF ORGANIC MATERIALS AND METALS: MECHANISMS AND APPLICATIONS. M. Koch, M. Lapczyna, K. Mueller, G. Padeletti*, M. Stuke, Max-Planck-Institut f. biophys. Chemie, Goettingen, GERMANY; *ICMAT-CNR, Monterotondo

The small penetration depth of 157 nm VUV laser light in organic materials implies low threshold removal with high efficiency often exceeding 1 monomer/photon. In addition, for some materials including PMMA, ultra-smooth surfaces [1] are left behind, which are perfect for applications such as ultra-sensitive optical diagnostics in transparent microfluidic polymer chips for applications including genome analysis and biotechnology. For metals, ablation with short laser pulses reduces thermal penetration effects during pulse duration [2]. 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 157 nm ablation of liquid mercury will be presented.
[1] G. Padeletti, M. Lapczyna, M. Stuke, MRS Proc. 544 (1999) 3-8
[2] S. Preuss, A. Demchuk, M. Stuke, Appl. Phys. A61 (1995) 33-37
[3] I. Zergioti, M. Stuke, Appl.Phys. A67 (1998) 391-395 and references therein

3:30 PM J5.5
LASER MICROMACHINING OF METALLIC MOLD INSERTS FOR REPLICATION TECHNIQUES. Wilhelm Pfleging, Andreas Meier, Thomas Hanemann, Herbert Gruhn, Karl-Heinz Zum Gahr, Forschungszentrum Karlsruhe GmbH, Institute for Material Research.

The rapid manufacturing of mold inserts for micro injection molding is realised by laser patterning of cemented carbides, alloy or carbon steel. The structuring 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 sidewalls of patterned grooves is detected. Additionally, a reaction layer is formed on the laser treated surface. With increasing laser power the surface roughness R_a of the reaction layer increases from 2 μm up to 6 μm. After wet chemical etching R_a decreases down to 1-2 μm, and this seems to be independent of the used laser power density. Excimer planarisation 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 nm per pulse. The resulting surfaces reveal a roughness of about 300 nm with no pores at the sidewalls. 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 the formation of a Ni-enriched interface layer and an oxide surface layer may 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 optimising the process strategy. Mold inserts are manufactured by laser patterning, and microstructures composed of polymers or ceramic-composites are successfully demolded by using the UV-RIM technique with aspect ratios up to 10 and a minimum surface roughness of R_a=300 nm.

3:45 PM J5.6
QUANTIFICATION OF MELT EJECTION 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 vaporisation and by the expulsion of molten material. The latter commonly arises as a result of the rapid build-up of gas pressure within the growing cavity as evaporation takes place, but the precise mechanisms responsible for the phenomenon are still unclear. The current work is aimed at gaining an insight into these mechanisms via measurements of the amount of material ejected from 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 material removed by melt ejection. These include 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 (mild steel, tungsten, lead, copper, aluminium, and nickel superalloys), drilled with a JK701 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 phenomenon is explored in the light of these results.

4:00 PM J5.7
SURFACE PROCESSING AND MICROMACHINING OF POLYIMIDE DRIVEN BY A HIGH AVERAGE POWER INFRA-RED 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 studies. The FEL 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 hole drilling and surface transformation of as-made and aluminized DuPont Kapton PMDA-ODA film.

4:15 PM J5.8
MICROSTRUCTURAL CHARACTERISATION OF ELASTOMER/CARBON COMPOSITE ABLATED WITH KrF EXCIMER LASER. Jean-Francois Silvain[1], Hiroyuki Niino[2] and Akira Yabe[2]. [1]Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)-CNRS, Université Bordeaux, Pessac, FRANCE, [2]National Institute of Materials and Chemical Research (NIMC), Tsukuba, Ibaraki, 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 produce 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 crystal. In particular, we are interested in surface modification of elastic 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 foils shows agglomeration of carbon nanometric particles (extended slabs 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 extended carbon slabs inside the molten area. Growth mechanism of the large cone-like structure can then follow to aggregate small cone-like microstructures in a thick molten layer upon repeated laser irradiation.

4:30 PM J5.9
EFFECTS OF EXCIMER LASER IRRADIATION ON MICROMACHINING OF GLASSES. Pin Yang, Eugene L. Venturini, Gilbert L. Benavides, 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 micro-systems. However, the amorphous nature of glass makes it difficult to create high aspect ratio features required in the micro-systems 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 damages. In this study we will report the

micromachining ability of three different glasses, including quartz, pyrex, and soft glass, using a 248 nm wavelength excimer laser. Defect density created by UV irradiation for different glasses will be characterized. A correlation between the defect density, UV absoption, ablation threshold, and machining ability will also be reported. Sandia is a multi-program laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

4:45 PM J5.10
OPTICAL ABSORPTION OF LASER DAMAGED FUSED SILICA. M.D. Feit, Z.L. Wu, A.M. Rubenchik, J.D. Natoli, L.M. Sheehan and M.R. Kozlowski, Lawrence Livermore National Laboratory, Livermore, CA.

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

SESSION J6/U8: JOINT SESSION:
LASER-BASED DEPOSITION OF OXIDES
Chairs: David P. Norton and John D. 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. Craciun and R.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 re-evaporation of volatile components. Unfortunately, most high quality PLD grown materials still require substrate temperatures in excess of 650°C. If one wants to lower the substrate temperature 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 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 and form ozone and atomic oxygen. In addition to the laser-assisted PLD technique, the UV source 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 Park, Yong Lee, John Budai, Stephen Pennycook, Gyula 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 formation of future generation metal-oxide-semiconductor device structures. Epitaxial oxides on metals 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 interfaces on semiconductors and metals using pulsed-laser deposition. The specific cases to be discussed include CeO_2 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 elucidate the epitaxial relationship between the film and crystalline substrate.
This research was sponsored by the U.S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

9:15 AM J6.3/U8.3
MAGENTIC AND MAGNETORESISTANCE PROPERTIES OF PULSED LASER DEPOSITED $La_{2/3}Ca_{1/3}MnO_3$ THIN FILMS ON SILICON. D. Kumar[1], A.K. Sharma[2], S. Chattopadhyay[2], J. Narayan[2], S.V. Pietambaram[1], Rajiv K. Singh[1], C.B. Lee[3], J. Sankar[3]. [1]Department of Materials Science and Engineering, University of Florida, Gainesville, FL, [2]Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, [3]North Carolina A&T State University, Greensboro, NC.

The fabrication of $La_{2/3}Ca_{1/3}MnO_3$ (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 growth 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 metallurgical 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 $\mu\Omega$·cm were obtained. In order to achieve epitaxial growth of LCMO films, MgO and $SrTiO_3$ films were used as intermediate layers between LCMO and TiN layers. The structural characterizations of single layered and multilayered structures were carried out using x-ray diffraction, transmission electron microscopy, and phi-scan 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 an optimized condition, are on par with the properties of LCMO films on conventional oxide substrates such as $LaAlO_3$ and $SrTiO_3$ in terms of paramagnetic to ferromagnetic transition temperature, insulator to metal transition temperature, and magnetoresistance ratio. The paper will present the details of growth and physical 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 KrF LASER ABLATION. Kenji Ebihara, Fumiaki Mitsugi, Tomoaki Ikegami, Kumamoto University, Department of Electrical and Computer Engineering, Kumamoto, JAPAN; Jagdish Narayan, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC.

KrF excimer laser ablation technique is applied to fabricate the ferroelectric $Pb(Zr_xTi_{1-x}O_3)$(PZT) capacitor on Si(100) substrate. The $YBa_2Cu_3O_{7-x}$(YBCO) bottom elecrode was deposited on the Si coated by YSZ buffer layer under the appropriate depositon conditions(laser fluence 2-3 J/cm^2, O_2 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 ferolectric properties of the remanent polarization 25 μC/cm^2 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 10^9 cycles for the decrease to 10 μC/cm^2 polarization.

9:45 AM J6.5/U8.5
PULSED LASER DEPOSITION OF EPITAXIAL $SrVO_3$ FILMS ON (100)$LaAlO_3$ AND (100)Si. P.W. Yip and K.H. Wong, Dept of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR CHINA.

Thin films of $SrVO_3$ have been grown on (100)$LaAlO_3$ and TiN buffered (100)Si substrates by pulsed laser deposition. The films were deposited in temperature range of 450°C - 750°C and under ambient oxygen pressure between 10^{-6} and 10^{-2}Torr. Their structural properties were characterized using a four-circle x-ray diffractometer. High quality $SrVO_3$ films were obtained at growth temperatures above 500°C without post annealing. Heteroepitaxial relationship of <100>$SrVO_3$‖<100>$LaAlO_3$ and <100>$SrVO_3$‖<100>TiN‖<100>Si were observed for films deposited at ≥550°C. X-ray photoelectron spectroscopic studies of the films suggest that the vanadium is mainly pentavalent. 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/U8.6
IMPOSED LAYER-BY-LAYER GROWTH OF COMPLEX OXIDES WITH PULSED LASER INTERVAL DEPOSITION.
Dave H.A. Blank, Guus Rijnders and Horst Rogalla, 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 reorganize. 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 ferromagnetic junctions.

11:00 AM J6.7/U8.7
GROWTH OF ZnO/MgZnO MULTIPLE QUANTUM WELL SUPERLATTICES ON SAPPHIRE BY PULSED LASER DEPOSITION.
A.K. Sharma, C. Jin, A. Kvit, J. Narayan, North Carolina State 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[1] high quality $Mg_xZn_{1-x}O$ alloy single crystal films on c-plane sapphire by pulsed laser deposition (PLD). The bandgap of these alloys was varied upto 4.27 eV by varying Mg content (x) to 34 at.%. Photoluminescence (PL) spectra from these films obtained at room temperature were very bright characteristic of excitonic nature of emission. This new materials system opens up enormous possibilities for optoelectronic devices such as truely solar blind detectors and uv lasers. In further pursuence of this material system, we have grown $ZnO/Mg_{0.34}Zn_{0.66}O$ multiple quantum well superlattices on sapphire by PLD. The well thickness was varied from 20-40 *Å* and the barrier thickness was kept constant in these heterostructures. The characterization of these superlattices was 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 were extremely bright and blue shifted from the corresponding ZnO band-edge PL value. The results are in agreement with the simple calculations performed assumimg 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 highly efficient opto-electronic devices based on ZnO.
[1]A.K. Sharma, J. Narayan, J.F. Muth, C.W. Teng, C. Jin, A. Kvit, and R.M. Kolbas, and O.W. Holland, Appl. Phys. Lett., 75, 22 Nov. (1999).

11:15 AM J6.8/U8.8
SINGLE QUANTUM WELL STRUCTURE OF MgZnO/ZnO/MgZnO ON C-PLANE SAPPHIRE.
Supab Choopun, Dan Chalk, Wei Yang, R.D. Vispute, S.B. Ogale, R.P. Sharma and T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD.

The single quantum well structures of MgZnO/ZnO/MgZnO were grown on c-plane sapphire substrate by pulsed laser deposition. Photoluminescence measurement was performed on these samples as a function of the well width. The quantum well width was varied by adjusting the deposition time of ZnO confined layer. Room temperature and 77 K photoluminescence were studied using continuous-wave He-Cd laser (325 nm) and pulsed N-laser (337 nm). From continuous-wave and pulsed photoluminescence spectra, we have observed a blue shift with respect to a thick ZnO reference sample when the well width was decreased. These results were fitting with calculation based on the simple square well model using effective mass of electron (0.24) and hole (0.59). By eliminating the well width parameter, the conduction band quantized-energy as a function 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/U8.9
DEVELOPMENT OF LSCO AND LNO OXIDE ELECTRODES FOR SENSOR PROTECTION DEVICES.
Malin Charoenwongsa, Kelly Buddin, Mailidil Sebastian and Robert Schwartz, Clemson University, Department of Ceramic and Materials Engineering, Clemson, SC.

Oxide electrodes play a key role in a variety of devices, including protection schemes for sensors that operate in the 3 - 5 μm and 8 - 12 μm ranges. One such protection device currently under development is an electrostatic shutter, which is driven into a closed condition 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 materials indicate that α may 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 $\mu\Omega$-cm may be obtained. These results suggest that it should be possible to achieve the required balance of sheet resistance and transparency for the development of the electrostatic shutter. However, target film thickness will be in the range of 15 - 25 nm.

11:45 AM J6.10/U8.10
COMPARISON OF TEXTURED AND EPITAXIAL ZnO FILMS.
Y.R. Ryu, Henry W. White, Univ of Missouri, Dept of Physics & Astronomy, Columbia, MO.

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
Chairs: Clinton B. Lee and Xiaoxing Xi
Thursday Afternoon, April 27, 2000
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 Neocera, 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 450C. Using PLD deposited PZT and CMR hetero -structures non-volatile memories have been made which show over an 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 complementary lower cost technique and schemes for operating the PED singly or in conjunction with PLD will be discussed.

2:00 PM J7.2
CARBON NITRIDE FILMS SYNTHESIZED BY COMBINED LASER ABLATION AND ION BEAM PROCESSING.
Z.Y. Chen, J.P. Zhao, T. Yano, T. Ooie and M. Yoneda, Shikoku National Industrial Research Institute, Takamatsu, JAPAN.

Carbon nitride films have been prepared by laser ablating a graphite target in nitrogen ion beam processing where the deposition 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 spectrum (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 in carbon nitride phase was ~30% and the films were found to be essentially amorphous. XPS analyses indicated that these films consisted of two carbon nitride phases. One phase had a stoichiometry of ~1.3 (N:C) which was near to that of C_3N_4 and was identified as a tetrahedral component. The other phase had a stoichiometry of ~0.2 which was equal to that of C_5N and was identified as predominantly an sp^2 bonded structure. XRD pattern showed the coexistence of α- and β- C_3N_4 in films. FTIR observed that most of chemical bonding between carbon and 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 is favorable to C_3N_4 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_3N_4.

2:15 PM J7.3
MECHANICAL PROPERTIES OF HARD COATINGS SYNTHESIZED BY LASER ABLATION METHOD. Ashok Kumar, M. Vedawyas, Department of Electrical Engineering, University of South Alabama, Mobile, AL; M. Shamsuzzoha, 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. Our research is focused on the development of carbide and nitride coatings by the Pulsed Laser Deposition (PLD) method. Thin film coatings 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 microscope techniques. The mechanical properties of the films were evaluated to measure the hardness and modulus values. Microlaminate made of alternate layers of TiN and TiB_2 films is likely to offer promises of exceptionally high hardness and modulii and, therefore, can be employed for future protective coatings. Single layer of TiN, TiB_2 and TiB_2/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 resulting data revealed that the elastic modulus and hardness of multilayer coatings are superior to monolithic coatings of either of the two constituent films. It is suggested that the smooth nature of the interface between TiN and TiB_2 is responsible for the improved hardness. This work was supported by NSF-DMII-9900459 grant.

2:30 PM J7.4
OPTIMIZATION OF THE PROCESSING PARAMETERS FOR PULSED LASER DEPOSITION OF NICKEL SILICIDE OHMIC CONTACTS ON SiC. C.J.K. Richardson, J.B. Spicer, The Johns Hopkins Univ, Dept of Materials Science and Engineering, Baltimore, MD; J.K. Hirvonen, J.D. Demaree, M.W. Cole, Army Research Laboratory, Weapons and Materials Directorate, Aberdeen Proving Grounds, Aberdeen, MD.

This research investigates the potential of pulsed laser deposition to create reliable high current ohmic contacts of Ni_2Si 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 (900°C) anneals that are 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 macroparticles. Macroparticle formation on the resulting films appear in the form of solidified droplets of the eutectic composition nickel silicide (3:1) 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 *J7.5
ADVANCES IN THE GROWTH OF ORGANIC THIN FILMS USING THE MATRIX ASSISTED PULSED LASER EVAPORATION (MAPLE) TECHNIQUE. A. Piqué, P.K. Wu*, J. Fitz-Gerald, D.B. Chrisey, R.A. McGill, V. Nguyen**, J.H. Callahan, B.J. Spargo and M.A. Bucaro, Naval Research Laboratory, Washington, DC. *Southern Oregon Univ., Ashland, OR, **Geo-Centers, Inc., Ft. Washington, MD.

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 accurate and precise thickness, are required for improved performance and component size reduction. NRL has developed a novel approach to process polymer and large organic or biomolecule thin films called MAPLE, for matrix assisted pulsed laser evaporation. The MAPLE technique is carried out in a vacuum chamber, and involves directing a pulsed laser beam (193, 213 and 248 nm; fluence = 0.01 to 0.5 J/cm^2) onto a frozen target (100 - 200 K) consisting of a solute polymeric 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/organic molecules coat the substrate. Thin uniform films (10-1000 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 electrospray mass spectrometry. Careful control of the processing conditions allowed the complex polymer/organic molecules to be transferred to the substrate as 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 J7.6
OPTIMIZATION OF PROCESSING PARAMETERS FOR DEPOSITING HYDROPHILIC POLYMER FILMS BY PULSED LASER DEPOSITION. James D. Talton, 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(lactic-co-glycolic acid) (PLGA), and poly(ethylene glycol) (PEG), as well as nondegradable 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 were characterized 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 particulate ejection 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 densities 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 process times on the order of minutes, (2) flexibility in depositing a variety of material such as various polymers and composite coatings, (3) control of coating thickness, morphology, molecular weight, and structure of desired films.

4:00 PM J7.7
PREPARATION OF SUPERHARD FUNCTIONALLY GRADED TETRAHEDRAL AMORPHOUS CARBON COATINGS BY PULSED LASER DEPOSITION. Q. Wei, S. Yamolenko, J. Sankar, Dept of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; A.K. Sharma and J. Narayan, Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

The internal compressive stress as large as 10 GPa has been the major stumbling block for preparation of relatively thick superhard tetrahedral amorphous carbon (Ta-C) 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 Ta-C 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 Ta-C. Nano-indentation measurements were performed on the coatings. Nanohardness as high as 65 GPa and Youngs modulus as large as 600 GPa were obtained for the functionally graded Ta-C 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 J7.8
CRYSTALLINE CHROMIUM CARBIDE THIN FILMS GROWN BY PULSED Nd:YAG LASER DEPOSITION. Kazuya Doi, Hiroharu Kawasaki, Satoshi Hiraishi and Yoshiaki Suda, Department of Electrical Engineering, Sasebo National College of Technology, Sasebo, 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 temparture (Ts) and methane gas pressure (P_{CH4}) on the properties of the CrCx thin films are discussed. Glancing-angle X-ray diffraction (GXRD) and a field-emission secondary electron microscope (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 $\geq$500°C is a polycrystalline thin film composed of Cr_3C_2 and Cr_7C_3. This polycrystaline thin film can be prepared independent of P_{CH4}. One of the growth mechanism of the Cr_7C_3 may be considered that the density of Cr atoms may be higher than that of C atoms in the plasma plume, and thus, the density of Cr atoms related to the surface reaction is higher than that of C atoms on the surface of the substrate.

4:30 PM J7.9
STRAIN AND OXYGEN STOICHIOMETRY EFFECTS IN $La_{2-x}Sr_xCuO_{4+\delta}$ THIN FILMS. Weidong Si and XiaoXing Xi, Department of Physics, The Pennsylvania State University, University Park, PA.

By growing $SrLaCuO_4$ buffer layers of different thickness on $SrTiO_3$ substrates, we were able to control the strain in the doped $La_2CuO_{4+\delta}$ thin films deposited epitaxially on them. When grown in molecular oxygen atmosphere, the undoped and lightly-doped $La_2CuO_{4+\delta}$ 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 $La_2CuO_{4+\delta}$ 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 $La_{2-x}Sr_xCuO_{4+\delta}$ 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 J7.10
THE PREPARATION OF NOVEL ZEOLITE FILMS VIA PULSED LASER ABLATION. Sharon E. Hogue, Lisa Washmon, Ashley Scott and Kenneth J. Balkus, Jr., The University of Texas at Dallas, Department of Chemistry, Richardson, TX.

Thin films and membranes of nanoporous 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 frits will be described. Zeolites such as UTD-1 require a UV adsorbing 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 silicalite on various substrates will be presented. The applications of these molecular sieve films in the areas of separations, catalysis, sensors and electrochromics will be outlined.