SYMPOSIUM Y

Advanced Optical Processing of Materials

April 22 – 23, 2003

Chairs

Ian W. Boyd
Dept of Electronic & Electrical Engr
Univ College-London
London, WC1E 7JE UNITED KINGDOM
44-20-7679-7307

Maria Dinescu
IFA-NILPRP, Romania
Atomistilor 1, Magurele
Bucharest, RO 76900 ROMANIA
004-021-4574470

Andrei V. Rode
Research School of Physical Science & Engr
Australian National Univ
Laser Physics Centre
Canberra, ACT 0200 AUSTRALIA
61-2-6125-4637

Douglas B. Chrisey
Code 6372
Naval Research Laboratory
Washington, DC 20375
202-767-4788

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as Volume 780
of the Materials Research Society
Symposium Proceedings Series

* Invited paper

SESSION Y1: PULSED LASER DEPOSITION
Chairs: Douglas B. Chrisey and Ian W. Boyd
Tuesday Morning, April 22, 2003
Olympic (Argent)

8:30 AM *Y1.1
PULSED LASER DEPOSITION OF OXIDES: RECENT ADVANCES AND CHALLENGES. David Norton, J. Sigman, Y.W. Heo, M. Ivill, V. Varadarajan, K.H. Kim, B.-S. Jeong, Y.W. Kwon, Y. Li, J.M. Erie, M. Jones, H. Bae, University of Florida, Department of Materials Science and Engr., Gainesville, FL; John Budai, Lynn Boatner, Oak Ridge National Laboratory, Oak Ridge, TN.

Pulsed laser deposition has been explored as a film growth technique for several years. Without question, its greatest impact has been on the growth of oxide materials. In this talk, we will discuss recent progress in utilizing pulsed-laser deposition in the growth of oxides materials for electronic applications, focusing on controlled doping of semiconducting and dielectric oxides. There is significant interest in semiconducting oxides in the areas of wide bandgap electronics, photonics, and spin-based electronics. In each case, control of dopants is critical. Dielectrics are needed as gate dielectrics for electric field-gated structures. We will discuss the unique advantages and limitations of pulsed laser deposition in addressing pertinent issues with these materials.

9:00 AM Y1.2
EVIDENCE OF METAL IMPLANTATION IN NANOCOMPOSITE THIN FILMS DURING PULSED LASER DEPOSITION. A. Suarez-Garcia, R. Serna, C.N. Afonso, J.-P. Barnes[a], A. Petford-Long[a], D. Hole[b], Instituto de Optica, C.S.I.C., Madrid, SPAIN. [a]Department of Materials, Oxford University, Oxford, UNITED KINGDOM; [b]School of Engineering, University of Sussex, Brighton, UNITED KINGDOM.

Pulsed laser deposition (PLD) is a thin film deposition technique that has shown to be suitable for the development of complex composite structures formed by metal NCs embedded in a dielectric matrix. The special features of the PLD leads to the presence of high kinetic energy species in the laser plasma (up to several hundred eV) that contribute to achieve films with good adherence and high density. In this paper we will show that high kinetic energy metal species can get implanted in depths up to 2 nm. The implications of metal implantation on the properties of metal NCs:dielectric thin films should be assessed. Nanocomposites formed by Bi NCs embedded in an amorphous Al_2O_3 matrix have been synthesized by alternating the deposition of amorphous Al_2O_3 (20 nm thick) and the deposition of Bi ($2x10^{15}$ at/cm^2). The laser energy for the ablation of the Bi target has been varied in the interval [0.5, 4] J/cm^2, while the growth conditions for the amorphous Al_2O_3 were kept constant. The number of pulses on the Bi target was modified together with the laser energy in order to deposit an approximately constant Bi content per layer. Plan view TEM images show the formation of Bi NCs whose morphological features exhibit a negligible modification as a function of the laser energy. In contrast, the cross section images evidence, in addition to the Bi NCs, a dark and apparently continuous dark layer appears underneath them, clearly visible for laser energy densities above 2 J/cm^2. This layer has been identified as being rich in Bi, and its distance from the surface increases as the laser energy increases. We explain the formation of the Bi rich layer in terms of implantation from the species originated in the laser induced plasma. The kinetic energy of the species and implantation range are determined.

9:15 AM Y1.3
CHARACTERIZATION OF SAMARIUM OXIDE FILMS DEPOSITED BY LASER ABLATION. Dongfang Yang, Dongfang Yang and Lijue Xue, National Research Council Canada, Integrated Manufacturing Technologies Institute, London, Ontario, CANADA.

Thin films of Samarium oxide is attractive for applications in microelectronic and opto-electronic devices due to its high dielectric constant and low likelihood of interaction with silicon substrate during processing to form silicides. In this paper, we will present results on the characterization of thin films of samarium oxide deposited by pulsed laser deposition (PLD) technique on silicon wafers of 75-mm diameter by KrF (248 nm) excimer pulsed laser ablation of a Sm2O3 target, in an oxygen environment. The substrates were heated during deposition at a temperature range of 25 to 680°C, while the oxygen pressure was set in the range 1 to 30 mTorr. The uniform coverage up to 75 mm diameter was obtained by rastering the laser beam over the rotating target, while the substrate was rotated simultaneously. Following deposition the crystalline character of the films was examined using X-ray diffraction and it was ascertained that the highest temperature deposited film was polycrystalline with monoclinic symmetry. The data for films deposited at low temperatures were either amorphous or partially crystallized amorphous structures with fine grain structures. The refractive index and extinction coefficient of the Samarium oxide films were simultaneously measured by spectral reflectance with wavelengths in the range of 250 to 850 nm. For all growth conditions, best fitting on the reflectance curves was achieved by assuming one layer on top of the silicon substrate. For l = 633 nm, refractive indices were in a range of 1.5 - 2.0 depending on the substrate temperatures and oxygen gas pressures.

10:00 AM Y1.4
PULSED LASER DEPOSITION OF SrS:Te THIN FILMS. James M. Fitz-Gerald and Jeff Hoekstra, University of Virginia, Department of Materials Science and Engineering, Charlottesville, VA; Philip D. Rack and Jason Fowlkes, University of Tennessee, Department of Materials Science and Engineering, Knoxville, TN.

The development of semiconductor based ultraviolet (UV) light sources is of critical importance for miniaturized ultraviolet light sources, which have application in several emerging areas such as biological agent detection and non-line-of-sight covert communications. To this end, a significant amount of research is currently being performed to extend the III-V nitride blue lasers and light emitting diodes into the ultraviolet region. In this paper we will discuss the ultraviolet emission of pulsed laser deposited thin films of SrS:Te grown at room temperature. In the bulk SrS has an indirect bandgap of ~4.32 eV. When SrS is doped with tellurium, ultraviolet emission occurs at 330 nm (for singlet) and 365nm (for Te-Te dimers) due to recombination from bound exciton states. The effect that the tellurium concentration has on the ultraviolet emission will be discussed along with results from microstructural (XRD and SEM), chemical (EDS) and optical (CL) characterization techniques.

10:15 AM Y1.5
CRYSTALLIZED $SrFeO_{3-x}$ FILMS DEPOSITED BY PULSE LASER ABLATION WITHOUT IN-SITU SUBSTRATE HEATING. Zhongke Wang, Takeshi Sasaki, Yoshiki Shimizu, Naoto Koshizaki, Naonoarchitectonics Research Center, AIST, Tsukuba, JAPAN; Mike Post, Institute for Chemical Process and Environmental Technology, NRC Canada, Ottawa, CANADA.

It is well known that $SrFeO_{3-x}$ is the functional material which exhibits good gas-sensing property. Crystallized $SrFeO_{3-x}$ ($0 \leq x \leq 0.5$) films have been deposited on SiO_2 glass by pulsed laser ablation without in-situ substrate heating using a third harmonic of Nd:YAG laser (355 mm in wavelength). X-ray diffraction pattern showed that the crystallinity of $SrFeO_{3-x}$ films strongly depended on the deposition pressure of Ar gas. The films deposited below 10 Pa were amorphous, and crystalline in brownmillerite phase from 10 to 200 Pa. The stoichiometry of metal components also closely related to the ambient pressure from X-ray fluorescence analysis. The films deposited at 30 Pa had the optimum stoichiometry, since the atomic ratio of [Sr]/[Fe] was about 1.05 near to 1 irrespective of laser energy. The atomic ratio [Sr]/[Fe] was above 1.1 below 10 Pa, and below 0.9 above 50 Pa. Thus the heavy A-site ions became rich compared to the light B-site ions in the deposited films at lower pressure as in the case of our previous study on $LaFeO_3$ and $BaTiO_3$ film preparation. Thus, there exist a proper pressure range for fabricating crystalline films with reasonable stoichiometry. Crystallized perovskite $SrFeO_3$ film can be obtained by post-annealing of the amorphous films at 300°C in air. This annealing temperature is quite low compared to typical crystallization temperature of 600°C. In summary, we can successfully get high quality crystalline $SrFeO_{3-x}$ film without in-situ substrate heating, and $SrFeO_3$ perovskite film by low temperature annealing of amorphous film obtained by laser ablation.

10:30 AM *Y1.6
HIGH PERFORMANCE TRANSPARENT CONDUCTING OXIDE FILMS GROWN BY PULSED LASER DEPOSITION FOR ORGANIC LIGHT-EMITTING DIODES. H. Kim, J.S. Horwitz, W.H. Kim, Z.H. Kafafi, and D.B. Chrisey, Naval Research Laboratory, Washington. DC.

High quality transparent conducting oxide (TCO) thin films have been grown by pulsed laser deposition (PLD) on glass, plastic and single crystal substrates such as sapphire, MgO and yttria stabilized zirconia (YSZ), for use in organic light emitting diodes (OLEDs). Critical electrode issues for the OLED are related to the optical transparency, electrical resistivity, work function and surface roughness of the TCO film. Our research has focused on improving the properties of the TCO film to increase the efficiency of the OLED. Films were deposited using a KrF excimer laser (248 nm, 30 ns FWHM) at fluences of 1 - 2 J/cm^2 at substrate temperatures ranging from 25°C to 600°C in oxygen pressures ranging from 1 to 100 mTorr. For In_2O_3:Sn, (ITO) films (100 nm thick) deposited on glass at 300°C in 10 mTorr of oxygen, a resistivity of $\sim 2 \times 10^{-4}$ Ω·cm was observed. The average film transmission in the visible range (400 - 700 nm) was about 90% and the film surface roughness was about 0.5 nm. The Hall

mobility and carrier density for ITO films (50 - 400 nm thickness) were observed to be in the range of 24 - 32 cm^2/V-s and 5 - 12 × $10^{20}cm^{-3}$, respectively. We have used the ITO films, deposited by PLD on glass, plastic and single crystal YSZ substrates, as the anode contact in OLEDs. ITO based devices showed an external quantum efficiency of about 0.8 - 1.2 % at 100 A/m^2. In this talk, we report our work on the synthesis, doping, and characterization of indium- and zinc-based TCO phases including In_2O_3:Sn, In_2O_3:Zr, ZnO:Al, ZnO:Ga, and ZnO:Zr. The properties of these films grown on various substrates will be compared and the use of these films as transparent anodes for OLEDs will be discussed.

11:00 AM Y1.7
HIGH REMANENT POLARIZATION IN LASER ABLATED $SrBi_2Nb_2O_9$ THIN FILMS. Rasmi R. Das, P. Bhattacharya, W. Perez, and Ram S. Katiyar, Physics Department, University of Puerto Rico, San Juan, PR.

Bismuth layered ferroelectric thin films, in particular $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ (SBN), have drawn much attention for nonvolatile memory applications. Pulsed-laser-deposition (PLD) technique was used to grow SBN thin films on platinized silicon substrates, at a laser energy density of 1.5 J/cm^2. Films showed a significant enhancement of ferroelectric properties with remanent polarization (P_r) of 25 $\mu C/cm^2$ and coercive field of 200 kV/cm. The ferroelectric property of the SBN thin films is strongly influenced by the film thickness. In this study we have deposited SBN thin films with thickness variation of 150-500 nm. Thin films were grown at a substrate temperature of 400°C with an oxygen pressure of 100 mTorr, followed by annealing at 750°C for 1 h. The dielectric constant of the films was found to be decreasing from 277 to 100 (at 100 kHz) with decrease in the film thickness and was attributed to the decrease in the grain size, observed by atomic force microscopy. The time and temperature dependent leakage current behavior of the films was studied in order to establish the dc current transport mechanism. Micro-Raman technique was used to study the thickness dependent phonon vibrational modes with a particular emphasis on the variation of the lowest transverse optical frequency. The detailed structural and electrical data of SBN thin films will be presented as a function of film thickness and PLD processing parameters. This work is supported in parts by NSF INT0097018 and NSF DMR 0079496 grants.

11:15 AM *Y1.8
PROPERTIES OF ZrO_2 THIN FILMS PREPARED BY LASER ABLATION. D.G. Matei[a], M. Morar[a], G. Epurescu[a], A. Ferrari[b], M. Balucani[b], G. Lamedica[b], G. Dinescu[a], C. Grigoriu[a], M. Dinescu[a]; [a]National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, ROMANIA; [b]INFM, University "La Sapienza", Rome, ITALY.

Zirconium oxide is a material with a large area of applications in electronics and electro-technical industry because of its high stability and dielectric constant of 20-30. These properties make possible the replacement of SiO2 for the gate dielectric material in metal-oxide-semiconductor (MOS) devices. ZrO2 thin films were prepared by laser ablation of Zr or ZrO2 targets in oxygen reactive atmosphere or vacuum, on various substrates (glass, sapphire, silicon, Pt coated silicon, quartz). The samples were investigated using X-ray Diffraction, Atomic Force Microscopy, Secondary Ion Mass Spectroscopy, optical absorption spectroscopy and electrical measurements. The influence of the deposition parameters, as laser fluence, oxygen pressure, substrate type and temperature and laser wavelength on the structure, composition and morphology of the deposited layers has been investigated. The nature of the plasma plume species and their distribution within the plasma volume have been studied by optical emission spectroscopy. The correlation between the plasma characteristics and the film properties is discussed. The quality of the interface substrate-ZrO2 film has been examined using high-resolution transmission electron microscopy (HRTEM) technique. A study regarding behaviour of dielectric constant and leakage current versus film and interface properties has been carried out.

11:45 AM Y1.9
A NEW TECHNIQUE FOR DETERMINING LASER POINTING STABILITY. Jeremy Gray, Petros Thomas, Xiangdong Zhu, University of California-Davis, Department of Physics, Davis, CA.

We describe an oblique-incidence optical transmissivity difference technique for determining the pointing stability of a laser. In this technique, we follow the angular drift of a monochromatic laser beam by measuring the relative changes in complex transmissivity through a fuzed quartz window for s and p polarized components of the beam, in response to angular drift. This method is shown in the present experiment to have the sensitivity to detect angular changes in the range of 2 microradians. To demonstrate the technique, we measured the angular drifts of two commercial intensity-stabilized He-Ne lasers.

SESSION Y2: FEMTOSECOND PROCESSING
Chairs: Maria Dinescu and Andrei V. Rode
Tuesday Afternoon, April 22, 2003
Olympic (Argent)

1:30 PM *Y2.1
SHORT LASER PULSES INTERACTION: COUPLING TO SOLID, PLASMA IGNITION AND EXPANSION, PARTICULATES FORMATION AND NANOSTRUCTURES DEPOSITIONS. Ion. N. Mihailescu, Eniko Gyorgy, and Carmen Ristoscu, Institute of Atomic Physics, Lasers Department, Bucharest-Magurele, ROMANIA; Costas Fotakis and Argyro Klini, Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser, Heraklion, Crete, GREECE.

We comparatively analyze the peculiarities of UV ultrashort (sub-ps) to ns laser pulses interactions with ceramics in vacuum and ambient gases. The characteristic features cover the crater formation, the ignition, development and propagation of plasma with special emphasis on temperature density, formation and transport of particulates, and the growth of crystalline nanostructures on different substrates. A particular attention will be paid to the case of KrF* (λ = 248 nm) laser radiation and AlN targets. The obtained thin structures were investigated by complementary techniques (electron microscopy, X-Ray Diffraction, nuclear techniques) and the results have been correlated with plasma temperature, density and expansion velocity data (Optical Emission Spectroscopy, Time-of-Flight Mass Spectroscopy). The obtained data will be discussed as against particulates formation (of micro and nano dimensions) either on target surface or during the plasma development. Special preparation techniques and supplementary processing methods applied in-situ will be proposed for obtaining particulates of controlled dimensions or to get their complete elimination. For example, our studies have shown that a key parameter in obtaining a low or zero density of particulates of any dimension is the very good quality of the laser beam incident on the target surface. The investigated experimental situations will be step-by-step discussed in comparison with similar experimental evidence recorded under the action of sub-ps and ns laser pulses.

2:00 PM *Y2.2
UNIQUE FUNCTIONAL MICRO/NANO-STRUCTURES CREATED BY FEMTOSECOND LASER IRRADIATION. M.H. Hong, B. Lukyanchuk, Z.B. Wang, J. Lam, S.M. Huang, D.J. Wu and T.C. Chong, Data Storage Institute, SINGAPORE.

Femtosecond laser is a versatile precision engineering tool to create unique functional micro/nano-structures, which are difficult or impossible tasks for other conventional laser sources and manufacturing systems. This ultrafast laser processing has the advantages of: extremely high peak power intensity, minimal or no heat affected zone (HAZ), nonlinear and multi-photon absorption. It can process almost all kinds of materials, especially to generate different microstructures inside the bulk transparent materials. It can also create nanopatterns on the substrate surface with the central part of laser beam energy. In this presentation, new applications of this laser in 3D optical data storage, semiconductor device singulation, photonics device fabrication and bio-engineering will be introduced. Theoretical background on the femtosecond laser interaction with materials will be discussed.

2:30 PM Y2.3
MOLECULAR DYNAMICS SIMULATIONS OF NUCLEATION AND CRYSTALLIZATION PROCESSES DURING EXCIMER-LASER ANNEALING OF AMORPHOUS SILICON ON GLASS. T. Motooka, S. Munetoh, Lee Byoung Min and K. Nisihira, Kyushu University, Dept of Materials Science and Engineering, Fukuoka, JAPAN.

Poly-silicon (Si) thin film transistor (TFT) is a key component of liquid crystal display (LCD) panels. Recently, much attention is paid to system-on-glass LCD in which both LCD active-matrix switches and driving as well as controlling circuits are included in TFT on glass for the development of mobile multimedia devices. In order to realize such system-on-glass LCD, it is crucial to develop the method to grow high-quality crystalline Si on glass. The most popular method is to use excimer-laser pulse (10-20 ns) shots to anneal amorphous Si (a-Si) films on glass where crystal growth is initiated by rapid melting of a-Si and quenching of melted Si. Since crystallization occurs in very thin (50-100 nm) a-Si films within a few 100 ns, almost all experimental studies were carried out only after crystallization occurred. Although theoretical studies have been carried out to analyze the crystallization processes based on thermal diffusion equations, the detailed atomistic processes are not well understood. We have investigated atomic processes of nucleation and crystallization in excimer-laser irradiated thin Si films based on large-scale molecular-dynamics (MD) simulations using the Tersoff potential. First, MD cells composed of approximately 10000 Si atoms were heated to produce melted Si. Then, melted Si was quenched

under various supercooled conditions with various temperature gradients. It has been found that (1) nucleation initially occurs in the lower temperature region as expected, (2) the critical nucleation size can be estimated to be 2-3 nm, and (3) the surfaces of the crystalline nano-particles are predominantly {111}. Examples of atomic motions during crystallization following nucleation obtained by MD simulations will be shown by a movie.

2:45 PM Y2.4
PHYSICAL MECHANISMS RELATED TO NANOSCALE FEMTOSECOND LASER MACHINING. A.J. Hunt, P.P. Pronko, G.A. Mourou, K. Beach, Y.N. Picard, V. Srivatsan, A.P. Joglekar, and S.M. Yalisove, Center for Ultrafast Optical Sciences, University of Michigan, Ann Arbor, MI.

Recent results from A.J. Hunt's laboratory at the Center for Ultrafast Optical Sciences at the University of Michigan have suggested that femtosecond machining features may be produced which are an order of magnitude smaller than any other reported values. He showed that single 600 fs pulse of 527 nm light could produce a hole with diameter ~20nm by focusing the light (with a high numerical aperture objective) on the backside of a glass plate. We will present results that illuminate the physical mechanism of the material-ultrafast light interaction under these conditions. This is accomplished by studying a single crystal material (Si). The light is focused through the material in order to avoid refractive index mismatch as the beam comes to focus. To accomplish this in Si, which absorbs light in the visible range, we will use a 1054 nm laser and wafers thinned to 8 microns. Si of this thickness will transmit 1054 nm light. Transmission electron microscopy data from areas adjacent to a machined feature will be shown and some physical mechanisms will be discussed.

3:30 PM *Y2.5
ULTRASHORT PULSE MICROMACHINING AND NEW FEMTOSECOND LASER TECHNOLOGIES. Boris N. Chichkov, Laser Zentrum Hannover e.V., Hannover, GERMANY.

The field of femtosecond laser material processing has rapidly evolved during the last years. Now using femtosecond laser pulses, one can produce high-quality patterning of solids, high-speed drilling of targets, complicated 2D and 3D microstructuring of materials, etc. In this presentation, I will report on our recent progress in femtosecond material processing, nanostructuring, and fabrication of photonic devices. I will also provide a discussion of most promising femtosecond laser technologies.

4:00 PM Y2.6
GENERATION AND FORMATION OF GOLD NANOPARTICLES WITH SPATIAL CONTROL BY TWO-PHOTON FEMTOSECOND LASER INTERFERENCE. Xuan-Ming Duan, Hong-Bo Sun, Koshiro Kaneko, Satoshi Kawata, CREST and PRESTO, JST (Japan Science and Technology Corporation) and Department of Applied Physics, Osaka University, Osaka, JAPAN.

A simple strategy for generating metallic nanoparticles and forming feature in polymer matrix with a spatial control in micrometer/nanometer scale has been proposed and successfully demonstrated by combination of two-photon photoreduction and femtosecond laser interference technique has been demonstrated. The simultaneous spatially controlling generation and formation of metallic nanopartciles with different size were controllable by designing interference patterns and varying laser intensity and exposure time. This strategy provides a simple and rapid approach for creating templates with designed spatial distribution of the nanoparticles, which is favorable for current microelectronics technology. This method also can be utilized in developing mass production processes for future nanodevices.

4:15 PM Y2.7
CHARACTERIZATION AND MECHANISMS OF POINT DEFECT PRODUCTION OF ALKALI SILICATE GLASSES WITH ULTRAFAST LASER IRRADIATION. Tom Dickinson, Sergey Avanesyan, and Steve Langford, Washington State University, Dept. of Physics, Pullman, WA; Larry Pederson, Pacific Northwest National Laboratory, Richland, WA.

It is commonly known that X-ray, gamma-ray, and electron beam irradiation of alkali containing silica glasses readily produces coloration in the bulk due to point defect production. We show that nearly identical coloration is generated by 100 fs pulses of 800 nm irradiation at intensities well below the breakdown threshold. The coloration is highly non-linear (these glasses all become strongly absorbing at z~300 nm). The glasses studied to date include Na-, K-, and Li- tri-silicates as well as soda-lime glass. Absorption spectra of the irradiated glasses reveal that exposure to these ultrafast IR pulses yield broad band absorption from 300 nm -800 nm. The sites responsible for this absorption have been identified as a collection of trapped electron and trapped hole defects. The presence of non-bridging oxygens associated with the alkali are seen to be essential no coloration occurs in pure silica. We present time resolved absorption measurements to determine the kinetics of both defect formation and recovery relative to each laser pulse. Time scales of interest are surprisingly longmilliseconds to seconds and are attributed to electron and hole transport following multiphoton ionization. We compare these kinetics as a function of intensity and also with exposure at 400 nm and 267 nm.

4:30 PM *Y2.8
FEMTOSECOND PULSES AS A NEW PHOTONIC SOURCE FOR GROWING THIN FILMS BY PULSED-LASER DEPOSITION. Eric Millon, GPS, CNRS and Université Paris VI et VII, Paris, FRANCE; also at LSMCL, Université de Metz, Metz, FRANCE; Jacques Perriere, GPS, CNRS and Université Paris VI and VII, Paris, FRANCE; Olivier Albert, Jean Etchepare, LOA, CNRS and ENSTA, Ecole Polytechnique, Palaiseau, FRANCE; Chantal Boulmer-Leborgne, GREMI, CNRS and Université dOrleans, Orleans, FRANCE.

The femtosecond (fs) lasers display noticeable specificities compared with the nanosecond ones operating in the UV domain, and classically used for the pulsed-laser deposition (PLD) technique. The ultra-short laser pulses offer the feature of minimal thermal damage induced in the target material, and the very high intensities (10^{12-14} W/cm^2) available with fs lasers are likely to allow the ablation of any kind of materials, even wide band gap insulators. Multiphoton absorption, Coulomb explosion, and emission of energetic species lead thus to new phenomena during the PLD of thin films using such fs lasers. Indeed, a broad range of behaviours have been observed in the cases of metals (Ti, Al), semiconductors (Si, GaAs) and insulators ($BaTiO_3$, ZnO, AlN). We will present results concerning fs PLD, in order to correlate morphology, structure, composition and properties of the films with the experimental growth conditions, the nature of the target material, and the dynamic expansion of plasma plume. In the case of ZnO, smooth, dense and nanocrystalline films (10 to 30 nm crystallites) can be epitaxially grown on adequate substrates (i.e. sapphire). On the contrary, Ti and $BaTiO_3$ films are formed by the random stacking of aggregates (10 to 200 nm) leading to a non negligible surface roughness,. In addition, the chemical composition of fs PLD thin films of multicomponent compound (i.e. $BaTiO_3$) is not homogeneous, an enrichment in the lighter element being observed in the central part of the film. These properties are related to the phenomena taking place during the various steps of the process (laser-matter interaction, plasma formation, expansion) through time resolved emission spectroscopy and plume optical imaging measurements. Finally, the limitations of the use of ultra-short laser pulses for the growth of thin films will be discussed, in order to evaluate the future of fs PLD.

SESSION Y3: POSTER SESSION
PHOTONIC PROCESSING
Chairs: Douglas B. Chrisey and Ian W. Boyd
Tuesday Evening, April 22, 2003
8:00 PM
Golden Gate (Marriott)

Y3.1
NONLINEAR OPTICAL SPECTROSCOPY OF CADMIUM CHALCOGENIDE NANOCRYSTALS. J.T. Seo, Q. Yang, S. Creekmore, J. Mangana, J. Anderson, C. Pompey, and D. Temple, Department of Physics, Hampton University, Hampton, VA; X. Peng, J.L. Qu, W. Yu, and A. Wang, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR; A. Mott, US Army Research Laboratory, Adelphi, MD; M. Namkung, Nondestructive Evaluation Sciences Branch, NASA Langley Research Center, Hampton, VA.

The high nonlinear figure of merit and large nonlinear refraction of chalcogenide semiconductor nanocrystals are of great interest for optical power limiting applications. These applications include homeland security of human-eye and sensor protection against potential laser terror threats, and agile laser threats on the battle field, optical switching, and pulse shaping in OPO/OPG. The quantum confinement and the surface trapped state effects of nanocrystals are the possible origins of their large optical nonlinearity. High quality semiconductor nanomaterials were synthesized through colloidal methods, and evaluated nonlinear optical properties for optical power limiting applications. For CdTe nanocrystals with 3 min growth, the typical first exciton absorption peak and absorption band-edge are located at ~665 nm and ~700 nm. Their diameter is estimated to be ~5 nm. It is a strong bandgap shift compared to the band-edge (~863 nm) of bulk materials. Both the appearance of discrete energy-states and the blue-shift of CdTe nanocrystals are because of the strong quantum confinement. The nonlinear absorption

and nonlinear refraction of CdTe nanocrystals were evaluated with Z-scan nonlinear spectroscopy with a 1-ps Ti:Sapphire pulse laser at ~800 nm with a repetition rate of 82 MHz. The nonlinear refraction coefficient of CdTe in toluene (~8 x 10^{-5} mol/L) was estimated to be ~-1 x 10^{-13} m^2/W. With conservative evaluation, the nonlinear FOM of CdTe in toluene was estimated to be ≥200 at ~800 nm. The sample was placed at ~8 mm from the beam waist for effective optical power limiting. The incident laser beam through the sample was almost totally diffracted at values higher than ~0.8 GW/cm^2. The optical power limiting through the CdTe nanocrystal was mainly by the large nonlinear refraction and high nonlinear figure of merit. The additional nonlinear optical properties and optical power limiting effects of CdTe, CdSe, and CdS will be discussed.

Y3.2
PRODUCTION OF III-V NANOCRYSTALS BY PICOSECOND PULSED LASER ABLATION. M.H. Wu, R. Mu, A. Ueda, and D.O. Henderson, Fisk University, Department of Physics, Nashville, TN.

InAs and GaAs nanoparticles have been produced by picosecond pulsed laser ablation of bulk targets in the presence of an inert backing gas. Atomic force microscopy measurements show particles ranging in size from one to ten nm. Particle size can be controlled by a combination of laser pulse energy, backing gas pressure and distance of the sampling site from the plume center. Stoichiometry of the targets, determined by Rutherford backscattering measurements, are typically preserved within a few percent. Optical absorption and raman scattering data are consistent with models of quantum confined, crystalline particles.

Y3.3
N DOPED ZnO THIN FILMS PREPARED BY PULSED LASER ABLATION IN NO AMBIENT GAS. Tamiko Ohshima, Tomoaki Ikegami, Kenji Ebihara, Kumamoto Univ, Dept of Electrical and Computer Engineering, Kumamoto, JAPAN; Raj Kumar Thareja, Indian Institute of Technology, Dept of Physics, Kanpur, INDIA; Yoshiaki Suda, Sasebo College of Technology, Dept of Electrical Engineering, Sasebo, JAPAN.

Zinc oxide (ZnO) is II-VI semiconductor having unique properties of direct band gap (3.3 eV) at room temperature (RT) and a large excition binding energy (60 meV). ZnO has a good candidate material for optoelectrical applications such as the ultraviolet (UV)-blue light emitting diodes (LEDs), laser diodes (LDs) and phosphorescent displays. ZnO naturally indicates n-type conduction due to the interstitial zinc atoms and oxygen atom vacancies in the lattice. It is necessary to fabricate p-n homojunctions in order to realize ZnO photonic devices. There are some reports on attempts to fabricate p-type ZnO using various techniques so far. Here we have also attempted to fabricate p-type ZnO thin films by pulsed laser deposition technique. We proposed nitrogen (N) atoms as the acceptor dopant. In this study N atoms were supplied by dissociating pure nitric oxide (NO) gas during the film deposition. NO is easy to be dissociated into N and O because of dissociation energy lower than nitrogen (N_2), ammonia (NH_3) and nitrogen dioxide (NO_2) gases. We have prepared N doped ZnO thin films under various NO gas pressures form 50 to 300 mTorr. The N doped ZnO thin films were deposited on quartz glass substrates at laser fluence of 2 J/cm^2 and substrate temperature of 400°C. Structural and optical properties of grown films were investigated using XRD, UV-visible light transparency, AFM and XPS. The p-/n- conduction type was studied by Hall measurements using van der Pauw method. All films in this experiment showed (002) c-axis orientation and optical band gap of 3.15-3.22 eV. The N doped ZnO thin film deposited at NO gas pressure of 200 mTorr indicated p-type conduction having high resistivity and low carrier concentration.

Y3.4
INFLUENCE OF La ADDITION ON PLZT THIN FILMS PREPARED BY PULSED LASER DEPOSITION. S. Canulescu, G. Epurescu, N. Scarisoreanu, C. Grigoriu, M. Dinescu, National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, ROMANIA; F. Craciun and P. Verardi, CNR-IDAC, Rome, ITALY; C. Galassi and A. Costa CNR-IRTEC, Faenza, ITALY.

La-modified lead zirconate titanate (PLZT) belongs to the family of perovskite relaxor ferroelectrics which exhibit a broad phase transition, depending on the La content. (Pb1-xLax(Zr0.65Ti0.35)O3 (PLZT) thin films have been deposited by pulsed laser ablation of targets with La content of 1, 2, 9 at.%. A parametric study has been performed to show the influence of the laser wavelength (266 nm, 355 nm and 532 nm), laser fluence (4-5 J/cm2) and substrate temperature (550-6500C) on the dielectric constant behavior. Different configurations substrate-bottom electrode have been also checked: Pt coated Si, LSCO/MgO, LSCO/Si. The films composition was studied by Secondary Ion Mass Spectroscopy (SIMS), their morphology by X-Ray Diffraction (XRD) techniques and surface topography by Atomic Force Microscope. The complex dielectric permittivity was measured at different frequencies using a HP 4194A impedance bridge, while the samples were placed in a Delta Design 9023 test chamber which could be operated between -180 and 310°C. Ferroelectric hysteresis measurements were performed at different temperatures using a Radiant Technologies RT 66A device.

Y3.5
MECHANICAL PROPERTIES AND MORPHOLOGY OF PULSED-LASER DEPOSITED $BaTiO_3$ THIN FILMS. Jie Xu, Dan Durisin and Greg Auner, Wayne State Univ, Dept of Electrical and Computer Engineering, Detroit, MI.

$BaTiO_3$ thin films were grown on Si(100) substrate by KrF pulsed laser deposition (PLD). The process parameters, such as gas pressure, substrate temperature, and laser fluence were varied in order to investigate their influence on the microstructural and mechanical properties. The films were characterized by X-ray diffraction (XRD), UV/VIS/NIR spectrometer, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The hardness, Young's modules and scratch testing of $BaTiO_3$ films were measured using nano-indenter. The stoichiometric $BaTiO_3$ films having uniform polycrystalline grains were grown. At higher fluences, the defects and particulates were generated. The particulate size and density were increased with tighter laser focus. Also, the results from dynamic scratch test indicated that the films with good adhesion were deposited at moderate laser fluence.

Y3.6
OPTICAL CHARACTERIZATION OF NANO-THIN FILMS USING PULSED LASER DEPOSITION. Kai Dou and Allen Alpblett, Department of Chemistry, Oklahoma State University, Stillwater, OK; Todd Mcfarland and Thomas Collins, Education Research Foundation, Oklahoma State University, Stillwater, OK.

Pulsed laser deposition technique was used to prepare thin films and coatings of metals, polymers, and tribological materials such as carbon, ZnS, SiC, B4C, TiN, Ti, Polyethylene, Polystyrene, etc. aimed at the improvement of mechanical and optical properties. Surface morphology by the scanning electron microscopy (SEM) confirms smooth coatings have been successfully achieved, and mechanical properties of these coatings such as antiscratch and adhesion have been examined with the tape, pneumatic adhesion tensile testing instrument (PATTI), and scratch adhesion tester. B4C, TiC, and TiN coatings deposited by subpicosecond-regime PLD were much smoother than nanosecond-regime PLD coatings, consistent with the transfer of smaller particles. MoS2-based coatings exhibited good adhesion; PLD coatings exhibit excellent coating-substrate interfacial toughness in the Rockwell C-Brale indentation tests. The results obtained offer significant potential for the development of novel coatings of interest to the various coatings industries. The ultrahard materials, B4C, TiC, and TiN, are useful as protective coatings. Specific industry applications include aerospace, lubricant-free machining, and moving mechanical (e.g., gearing and bearing) assemblies. The technique established here is promising for fabrication of nanostructures such as heterojunction, quantum wells (QWs), multi-quantum wells (MQWs), and superlattices (SLs) and related light emitting diodes (LEDs), laser diodes (LDs), and detectors demanded in optical, photonic, and optoelectronic fields.

Y3.7
PHOTOINDUCED LOW REFRACTIVE INDEX PATTERNING IN A PHOTOSENSITIVE HYBRID MATERIAL. Jang-Ung Park, Eun-Seok Kang, Byeong-Soo Bae, Lab of Optical Materials and Coating, Dept of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, REP. OF KOREA.

Over the past several decades, the interest has increased in the use of photosensitive materials which show changes in the refractive index or surface modulations of a medium upon light illumination for the wide range of applications including diffractive optical elements, optical recording, and antireflective coatings etc. Those photoinduced changes of general photosensitive materials such as germanium silicate glasses and azo-polymers are not large. In this research, a new organic-inorganic hybrid material system, that created photoinduced reduction of refractive index as well as volume contraction, was developed so as to be patternable. Whereas previous hybrid materials show the photoinduced increase in refractive index, this hybrid material creates the significant decrease in refractive index using decomposition of organic methacryl groups on light irradiation. The reduction of refractive index measured with a prism coupler was about 0.045, particularly exhibiting a low refractive index value of 1.385, comparable to the indices of perfluorinated polymers (for example, the index of PTFE® 1.38). We investigated the structural change of the hybrid material on light irradiation by FT-IR and energy dispersive X-ray spectroscopy (EDS) and the surface roughness change by AFM.

From the measurement of contact angle and dielectric constant, we knew that the surface of hybrid material is very hydrophobic and dielectric constant decreases significantly by light illumination. We also carried out direct imprinting of the organic-inorganic hybrid material without any further steps (wet etching, thermal curing, or UV fixing), using the volume contraction on light irradiation. This photosensitive hybrid material, therefore, can be applied in the fields of antireflective coatings with superhydrophobic surfaces using surface relief gratings and in the production of low dielectric materials.

Y3.8
PULSED LASER DEPOSITION IN A ZINC ALLOY CORROSION STUDY. Roberto Guerrero-Penalva, Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, BC, MÉXICO; M.H. Farias and L. Cota-Araiza, Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, BC, MÉXICO.

A significant improvement in corrosion resistance of the protecting oxide of alloys has being observed when adding small amounts of reactive elements, such as yttrium, this effect has been called reactive element effect (REE). Little or nothing has being published about the REE produced improvements on alloys based on magnesium or zinc. Several particular mechanisms, which can be applied to certain specific cases, have being proposed. However, the general mechanism of the REE has not being determined yet. The REE can be obtained by incorporating either metallic yttrium or a dispersion of oxide particles. The beneficial effect could be obtained by means of surface coatings of the reactive element.To our best knowledge, nothing has being published on regards to REE studies performing deposition by means of pulsed laser deposition (PLD). This technique, although relatively expensive for commercial purposes, presents advantages for studying the REE. The amount of deposited material can be easily controlled. In this work, we study the interaction of yttrium oxide films deposited by PLD with the two solid solutions (h and a) present in the alloy Zn-22Al-2Cu named Zinalco®. The PLD technique and x-ray photoelectron spectroscopy (XPS) could be used advantageously in the REE studies, due to their ability to control and monitoring small amounts of material deposited which permit to detect the preferentially adsorbing sites in the different phases of binary alloys. The yttrium oxide superficially deposited promotes enrichment in the aluminum concentration after annealing at 120°C. The mechanism by which the reactive element produce its effects is explained by the preferential interaction among the active sites related to the zinc rich phase and enhancing aluminum movement toward the surface where it is oxidized and the protection film formed.

Y3.9
MONITORING ION SPUTTERING OF NIOBIUM (110) USING AN OBLIQUE INCIDENCE REFLECTIVITY DIFFERENCE TECHINQUE. Petros Thomas, Xiangdong Zhu, University of California, Dept of Physics, Davis, CA.

We studied ion sputtering of Nb(110) surface from 300K to 1100K with an oblique-incidence optical reflectivity difference technique (1). The results are compared with previously reported low energy electron diffraction (LEED), low energy ion scattering (LEIS), and scanning tunneling microscope (STM) results. We found that the damage, as observed by the optical reflectivity difference signal, saturates at a level which depends on the sputtering temperature. For lower sputtering temperatures (from 300K to 700K), qualitatively, the optical signal is similar for different temperatures and can be explained as a three-dimensional removal (pit formation by stacking of vacancy islands into each other); in agreement with recent STM results (2). For higher temperatures (above 900K), two-dimensional removal (layer-by-layer removal) sets in and the optical signal differs significantly from the lower temperature behavior. Expressions are derived to explain surface damage and its relationship to the optical reflectance difference signal in terms of the optical polarizability of additional step edge atoms due to sputtering.
1. X.D. Zhu, E. Nabighian, Appl. Phys. Lett. 73, 19 (1998) 2736
2. M. Kalff, G. Comsa, Th. Michely, Surf. Sci. 486 (2001) 103.

Y3.10
AFM ANALYSIS OF FRACTAL STRUCTURES IN SILVER THIN FILMS. Zhenjia Wang, Lewis Rothberg, Hui Du and Todd Krauss, Department of Chemistry, University of Rochester, Rochester, NY.

There is strong interest in designing metallic films to exhibit strong surface enhanced optical nonlinearities. Fractal structures have been applied to two-photon fluorescence and surface enhanced Raman scattering. Giant enhancement of the electromagnetic field is associated with excitation of surface plasmon oscillations. This excitation is highly localized in fractal structures since they do not possess translational symmetry. Here, we analyze structures of silver films made in various ways using an AFM to measure surface roughness and determine whether fractal structures are obtained. We find that evaporated films are characterized by Hausdorff dimension D = 1, in agreement with previous STM measurements. We study films made using silver nanoparticles deposition from solution under various conditions in the same way and obtain films exhibiting fractal dimension D = 1.5 - 1.6 in 100 nm - 500 nm domains. We demonstrate the utility of these with surface Raman measurements.

Y3.11
OBLIQUE-INCIDENCE REFLECTIVITY DIFFERENCE STUDY OF ADSORPTION, GROWTH AND DESORPTION OF XENON ON NIOBIUM(110). Petros Thomas and Xiangdong Zhu, University of California at Davis, Dept of Physics, Davis, CA.

We studied adsorption, growth and desorption Xe on Nb(110) using an in-situ oblique-incidence reflectivity difference technique and low energy electron diffraction (LEED) from 32 K to 160 K. The results show that Xe grows a (111)-oriented film after a transition layer is formed on Nb(110). The transition layer consists of three monolayers. The first two monolayers are disordered with Xe-Xe separation significantly larger than the bulk value. The third monolayer forms a close packed (111) structure on top of the tensile-strained double layer and serves as a template for subsequent homoepitaxy. The adsorption of the first and the second monolayers are zeroth order with sticking coefficient close to one. The third monolayer is formed with adsorbates sticking to edges (perimeters) of islands. Above the third layer, growth of the Xe(111) film on the transition layer proceeds in a step flow mode from 54K to 40K. At 40K, an incomplete layer-by-layer growth is observed while below 35K the growth proceeds in a multilayer mode. We estimated activation energy of desorption for the second layer as $\sim$0.3 eV (6.84 kcal/mole) and activation energy of desorption for the top subsequent layers (above the second layer) as $\sim$0.15 eV (3.42 kcal/mole).

Y3.12
HIGHLY COLLIMATED LOW ENERGY BROAD BEAM ION SOURCE. Erik K. Wählin, Veeco Instruments, Fort Collins, CO.

A new ion beam accelerator system is presented that drastically reduces the ion beam divergence of current broad beam ion sources used in industrial applications. The new system, which employs a four grid multi-aperture accelerator system, has been shown to reduce the ion beam divergence angle by more than a factor of two, when compared to current two and three grid ion accelerators. This demonstrated reduction of the ion beam divergence angle has important implications for surface modification of materials that are sensitive to the ion impact angle. This includes ion beam etch (IBE) applications where collimated ion beams are desired for pattern transferring of high aspect features and for crystal alignment applications. Collimated beams have been shown to align both inorganic and organic surfaces for liquid crystal displays (LCD). They are also used in ion beam assisted deposition (IBAD) of the in-plane textured yittria stabilized zirconia (YSZ) buffer layer necessary for proper alignment of superconducting $YBa_2Cu_3O_7$ (YBCO) crystals. Highly collimated ion beams are also important for ion beam deposition (IBD) where the confinement of the ion beam to the sputter target without over spray reduces contamination in the deposited film. Data will be presented for 4-grid accelerator systems used on 6 x 66cm and 6 x 110cm RF linear ion sources suitable for large area processing and on a 16cm RF round ion source used for high rate ion beam sputter deposition. Beam collimation results will be presented for operation at beam energies of 250eV - 1,250 eV, and beam currents up to 800mA.

Y3.13
GROWTH OF ZIRCONIUM CARBIDE AND LANTHANUM HEXABORIDE FILMS BY PULSED LASER DEPOSITION FOR FIELD EMISSION TIP COATING APPLICATIONS. V. Cracuin, J.M. Howard, N.D. Bassim, T.J. Anderson, and R.K. Singh, University of Florida, Gainesville, FL.

Thin films of zirconium carbide and lanthanum hexaboride have been deposited by the pulsed laser deposition technique and analyzed for field emission tip coating applications. Structural information for the films was determined by x-ray diffraction, grazing incidence x-ray diffraction, and transmission electron microscopy. The thickness and interfacial roughness were investigated by x-ray reflectivity and variable angle spectroscopic ellipsometry. Surface morphology of the films was characterized by atomic force microscopy. Chemical information was obtained by x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Analysis of the structural and chemical data was completed and compared to the current emission properties of coated tips. This research was conducted to develop a definitive link between the current emission properties and the various morphological properties of the film coatings as they are affected by processing parameters such as laser fluence, deposition ambient pressures, and deposition temperature.

SESSION Y4: LASER PROCESSING OF BIOPOLYMER, POWDERS, AND MATERIALS
Chair: David Paul Norton
Wednesday Morning, April 23, 2003
Olympic (Argent)

NOTE EARLY START

8:00 AM *Y4.1
ULTRAFAST LASER DEPOSITION OF CHALCOGENIDE GLASS FILMS FOR LOW-LOSS OPTICAL WAVEGUIDES.
B. Luther-Davies, Y. Ruan, M. Samoc, and A.V. Rodem, Australian Photonics Cooperative Research Centre and Laser Physics Centre, Research School of Physical Sciences and Engineering, the Australian National University, Canberra ACT, AUSTRALIA.

Ultra-fast pulsed laser deposition was used to successfully deposit atomically smooth 5 micron thick As_2S_3 and $As_{24}Se_{38}S_{38}$ films. The as-deposited films were photosensitive at wavelengths close to the band edge and waveguides could be directly patterned into them by photo-darkening using an Argon ion or frequency doubled Nd:YAG laser. The linear and nonlinear optical properties of the films were measured as well as the photosensitivity of the material. The optical losses in photo-darkened waveguides were <0.2 dB/cm at wavelengths beyond 1200nm and <0.1 dB/cm in as-deposited films. The third order nonlinearity was measured using both four-wave mixing and the z-scan technique and varied with wavelength from 100 to 400 times fused silica ($n_{2,Silica}$ ~3x10−16cm^2/W) between 1500nm and 1100nm with low nonlinear absorption.

8:30 AM *Y4.2
ULTRASHORT LASER PROCESSING FOR MATERIALS MICROSTRUCTURING. Ioanna Zergioti, Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser, Heraklion, GREECE.

Two complementary methods for fabricating microstructures of metals, oxides and biomaterials are presented, both utilizing femtosecond UV laser pulses. This direct, single-step material removal process is applied in two distinct configurations. The spatially selective, ablation of materials permits the direct microetching of high-quality surface-relief patterns. In addition, the direct, spatially selective transfer of the ablated material onto planar and non-planar receiving substrates provides a complimentary microprinting operation. Precise deposition of biological macromolecules, such as lambda bacteriophage DNA, BSA and epitope tagged GST proteins, on solid surfaces, are presented by means of femtosecond laser printing process in order to fabricate high density resolution patterns, for biosensors and multi-analyte assays. The microstructuring of Lithium Niobate single crystals using short UV laser modification for improved photonic devices and diffractive grating structures for soft X-ray optics by the micromachining of Si/Mo, Si/W multilayer, are also presented. The dynamics of the laser microprinting process was studied by means of time-resolved schlieren imaging technique. A comparative experimental study between fs and ns laser pulses and a theoretical description of both processes is also presented here. The ejected material was measured to be highly directional with narrow angular divergence under ultrashort pulse laser irradiation. The use of ultrashort pulses is advantageous for the optical processing of materials and opens up new application possibilities for the fabrication of high spatial resolution microstructures.

9:00 AM Y4.3
EFFECT OF OXYGEN STOICHIOMETRY IN ZnO:Al FILMS DEPOSITED ON ZnS:Ag ON CATHODOLUMINESCENT DEGRADATION LIFETIMES. M. Ollinger, V. Craciun, S. Nagore, and R.K. Singh, University of Florida, Dept. of Materials Science and Engineering, Gainesville, FL.

Using the atomic flux coating process (AFCP) the functionality of micrometer-sized phosphor particles can be enhanced to give their surface a different property from the bulk. The AFCP uses a 248 nm wavelength excimer laser which ablates a ZnO:Al target under various oxygen pressures (from 10-4 to 10-2 Torr). The ablated species or nanoclusters are then deposited onto the host particles that are being mechanically agitated to form discrete or continuous coatings (on the host particles) depending on the desired application. In this study, one of the major problems in the Field Emission Display industry, which is the formation of a non-luminescent "dead layer" on the surface of phosphor particles after prolonged exposure to the e-beam which reduces the cathodoluminescent efficiency, was addressed. To prevent the formation of this dead layer, zinc oxide doped with aluminum was used in the AFCP to coat the phosphor powder and shield the phosphor core from forming the non-luminescent layer. These coated phosphors showed dramatic increased cathodoluminescent lifetimes as compared to the commercially received ZnS:Ag phosphors. Transmission Electron Spectroscopy was used to determine the uniformity of the ZnO:Al coatings. Scanning electron microscopy and x-ray photoelectron spectroscopy were used to investigate the particles surface morphology and chemical composition. The results showed that the nano-scale coatings deposited at lower oxygen pressures, where the ZnO was oxygen deficient, reduced the reactions taking place on the surface of the phosphors. In the lowest oxygen partial pressure case (0.14 mTorr), at 1 C/cm, the as-received phosphor had degraded by 100% of its initial intensity as compared to the coated sample, which had only lost 20% of its initial intensity.

9:15 AM Y4.4
APPLICATION OF MATRIX ASSISTED PULSED LASER EVAPORATION METHODS FOR THE DEVELOPMENT OF BIODEGRADABLE POWDER COATINGS AND THIN FILMS. A. Mercado and J.M. Fitz-Gerald, University of Virginia, Department of Materials Science; R. Johnson and C. Fraser, University of Virginia, Dept. of Chemistry, Charlottesville, VA; J.D. Talton, Nanotherapeutics, Inc., Alachua, FL.

The ability to controllably deposit PLGA onto flat, curved surfaces in a quasi - dry environment while retaining native-like structure is of extreme importance to the medical and microelectronics communities. Current applications range from protective and conformal coatings for microelectronics to sustained drug delivery platforms in the pharmaceutical industry. In this research, biodegradable thin films of poly(DL-lactide-co-glycolide) (PLGA), were deposited onto flat (Si) and curved (particulate) substrates using a pulsed excimer laser, (l= 248 nm) with fluences ranging from 0.1 - 1.0 J/cm2 via the matrix assisted pulsed laser evaporation (MAPLE) technique developed at the Naval Research Laboratory. Based on their optical absorption and vapor pressure characteristics, acetone, and chloroform were used as solvents. Variations in laser energy, frequency and target chemistry were selected in order to explore maximum parameter space. Results will be shown from scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC).

9:30 AM *Y4.5
PULSED LASER DEPOSITION OF PULLULAN POLYMER THIN FILMS FOR CONTROLLED DRUG DELIVERY COATINGS.
R. Cristescu, G. Socol, I.N. Mihailescu, National Institute for Lasers, Bucharest-Magurele, ROMANIA; F. Sava, M. Popescu, National Institute of Materials Physics, Bucharest-Magurele, ROMANIA; I. Stamatin, University of Bucharest, Physics Department, Bucharest-Magurele, ROMANIA; M. Albulescu, National Institute for Chemical-Pharmaceutical R&D, Bucharest, ROMANIA.

There is an urgently need to develop controlled drug release biocompatible and biodegradable systems which can be programmed to release their active core for variable duration from 1-100 days in an aqueous physiological environments. The systems are comprised of a biological active agent encapsulated in a matrix of polysaccharide pullulan. We have deposited pullulan thin films by the Pulsed Laser Deposition technique using a KrF* excimer laser source (λ= 248 nm, $\tau \geq$ 20 ns). Our aim is to control the stoichiometry and thickness of a nanoscale polymer coating. The studies have been conducted to characterize the chemical structure and morphology of the pullulan thin films. The relationship between the properties of the deposited thin films and the deposition experimental parameters as resulting from our investigations will be reported.

10:15 AM Y4.6
CHARACTERIZATION AND IN VITRO PHAGOCYTIC UPTAKE BY PULMONARY MACROPHAGES OF NANOCOAT POLYMER-COATED PARTICLES. James Talton, Barbel Eppler, Margaret Davis, Nanotherapeutics, Inc., Alachua, FL; James Fitz-Gerald, University of Virginia Department of Materials Science, Charlottesville, VA.

Drug delivery systems utilizing microencapsulation and microparticle carriers have been shown to dramatically improve the bioavailability and release profiles via inhaled, nasal, and oral delivery. One and five micron inert particles were coated using the NanocoatTM microencapsulation process to investigate how different polymer coatings would interact in biological systems including protein adsorption and macrophage uptake in vitro. PLGA, PLA, poloxamer, and different molecular weight PEGs were tested and characterized using SEM, FTIR, NMR, and GPC. Protein adsorption was measured by incubation with fetal bovine serum or individual proteins with gamma-globulin and albumin and measured using the BCA protein assay. In order to examine differential serum protein binding in serum, adsorbed proteins were also analyzed by SDS-PAGE and densitometry was performed using NIH image. Uptake and cytotoxicity with 5-micron particles was tested with J774A.1 murine alveolar macrophages. Overall, poloxamer and PEG clearly bound less total protein from serum. BSA and gamma-globulin also showed a similar trend with reduced binding for poloxamer and PEG, as well as PLGA.

Increased uptake of PLGA-coated ZnS:Mn particles (3.1 particles/cell) by macrophages was observed compared to uncoated particles (2.0 particles/cell), while neutral-charged PEG-coated particles showed a reduced macrophage uptake (1.1 particle/cell). Overall, by producing powder formulations that provide controlled-release, in addition to controlling particle cell uptake, improved absorption of drugs may be developed for a variety of therapies.

10:30 AM Y4.7
SIMS STUDY OF PLUMES GENERATED FROM 355NM AND 266NM LASER ABLATION OF POLYMERS. P.M. Moran, N.L. Yakovlev, S.Z. Yow, Z.L. Li, Institute of Materials Research and Engineering, SINGAPORE; Y. Sun and E.J. Swenson, Electro Scientific Industries, Portland, OR.

Plumes generated by ablation of polymer targets using 3rd and 4th harmonic Nd:YAG lasers (355nm and 266nm wavelength respectively) under different atmospheres (air, N2, and He) were captured on an H-terminated silicon substrate. The chemical composition and distribution of the deposited ablation debris were measured using time of flight secondary ion mass spectrometry. Nitrogen containing compounds (NCCs) and oxygen containing compounds (OCCs) were found in plumes ablated in air but not in N2 and He environments. We suggest that the formation of NCCs and OCCs is due to thermal dissociation of O2 in the air and, thereafter, oxygen-assisted dissociation of N2 in a process known as the Zeldovich two-step mechanism. Based on this mechanism, the distribution of NCCs and OCCs can provide an indication of the lower-bound temperature within the plume. In air and nitrogen, plumes from 355nm wavelength ablation are hemispherical with distinct borders. In He they are mushroom-shaped without sharp borders. These shape differences are usually attributed to atmospheric pressure differences, however, since all our experiments were carried out under atmospheric pressure, the differences can be related to the reactivity and molecular weight of the gas. The target material also influenced the plume dynamics. For example, 355nm ablation of polycarbonate targets showed indications of a laser-supported detonation front, whereas ablation of polyimide (Kapton HN) under the same conditions did not. It is not yet clear why the plumes of two such chemically similar polymers should behave so differently. These experimental observations as well as ablation rates and differences in 355nm and 266nm plumes and ablation will be discussed.

10:45 AM Y4.8
THE MERGING OF ELECTRONIC AND BIOLOGICAL COMPONENTS AND SYSTEMS THROUGH LASER MICROFABRICATION. D.B. Chrisey, R. Modi, H.S. Kim, and B.R. Ringeisen, US Naval Research Laboratory, Washington, DC.

We have used laser micromachining and a novel laser forward transfer technique called MAPLE DW (Matrix Assisted Pulsed Laser Evaporation Direct Write) to interchangeably fabricate discrete electronic components directly on biological systems and biomaterials on electronic systems. The flexibility in processing these vastly different materials is as a result of the wide dynamic range of the laser-material interaction spanning from ablation to a soft desorption process. Thin metal films on plastic and sacrificial substrates were micromachined to make fractal-enhanced reflector antennae with surface mount active components. When deposited directly onto small biological systems such as adult honeybees, the antenna is used for radar tracking with harmonic discrimination. Similarly, MAPLE DW can be used to deposit arrays and patterns of biomaterials ranging from proteins to living cells onto passive and active electronic subsystems. The CAD/CAM ability to interchangeably process patterns of such disparate materials by laser processing is especially important for seamlessly interfacing electronic and biological functions.

11:00 AM Y4.9
BIOCOMPATIBILITY STUDIES OF NiTi FILMS. V.C. Dinca[a], R. Tanasa[b], C.Z. Dinu[a], A. Barbalat[a], C. Grigoriu[a], A. Dauscher[c], E.O. Bucur[a], M. Dinescu[a]. [a]National Institute for Laser, Plasma and Radiation Physics, Bucharest, ROMANIA; [b]Pasteur Institute S.A, Bucharest, ROMANIA; [c]Laboratory of Materials Physic (LPM), INPL, Nancy, FRANCE.

NiTi thin films have been deposited on different substrates, Si, Ti, Ti-6Al-4V by alternative pulsed laser deposition starting from high purity Ni and Ti targets. A parametric study has been performed to evidence the influence of the laser wavelength (266 nm, 355 nm, and 532 nm), laser fluence (3-5 J/cm2), substrate temperature (25-350°C) and number of subsequent laser pulses on each target on thin film properties. X-ray diffraction, Scanning Electron Microscopy, Secondary Ions Mass Spectroscopy and Atomic Force Microscopy have been used to characterize the chemical composition and the surface topography of deposited layers. In order to investigate the biocompatibility of the nitinol, we have tested the assumption that cells attach during the culture period on the surface of NiTi layers deposited on Si, Ti, Ti-6Al-4V substrates. Vero and OTE animal cell lines dispersed into MEM (Eagle) solution containing 8% fetal bovine serum, at 370°C, have been used for tests. The cells cultured on the films deposited on Si substrates do not survive. After 4 days it is noticed an accentuated alkaline medium and the cells die due to the non-compatible surface of Si (the surface was not completely covered by NiTi). These cultures survive on the NiTi films grown on Ti and Ti-6Al-4V substrate; during the tests, after 5 days it is noticed noncytotoxicity of NiTi to Vero and OTE animal cell lines in vitro, the same characteristics being maintained after 25 days of testing with Giemsa coloration as well as after a direct microscopic examination. Earlier studies are in agreement with our present results and support the conclusion that NiTi is a good candidate as biocompatible material.

11:15 AM Y4.10
X-RAY STANDING WAVES - A FUTURE TOOL TO INFLUENCE STRUCTURE FORMATION ON SUB-NANOMETER SCALE. Dirk C. Meyer and Peter Paufler, Institute for Crystallography and Solid State Physics, Dresden University of Technology, Dresden, GERMANY.

The use of X-ray interference is now established for 90 years as substantial procedure for structural analysis. Almost unpredictable new possibilities can be expected by a future use of interference phenomena of X-rays as a tool to influence structure formation on sub-nanometer scale. Thereby X-ray standing waves (XSW), to be formed in case of interference of coherent X-rays, are of special importance. These XSW embody non-thermal periodic power density distributions, whereby the spatial period, so in case of the excitation of XSW by crystal lattice interferences, can be tuned exactly to values of atomic spacings in crystal lattices. Various methods for the excitation of XSW will be discussed, regarding their suitability as structure-chemical tools. In particular for prospective customers in crystal growth and layer deposition the potential of substrate-independent X-ray standing wave assisted deposition and growth (XSWDG) will be outlined. Apart from an overview on relevant experimental indications reported so far, the possibilities for new photo- chemistry, physics and biology by purposeful influencing reactions on a sub-nanometer scale will be pointed out.

11:30 AM Y4.11
SYNTHESIS OF PHOTOSENSITIVE ORGANIC-INORGANIC HYBRID POLYMERS VIA ANHYDROUS SOL-GEL PROCESS FOR INTEGRATED OPTICS. Xinshi Luo, Congji Zha, Barry Luther-Davies, Australian National Univ, Laser Physics Centre, Research School of Physical Sciences and Engineering, Canberra, ACT, AUSTRALIA.

Photosensitive organic-inorganic hybrid polymers were synthesised for integrated optical and optoelectronic devices by a non-hydrous sol-gel process of hydrolysis/condensation of 3-methacryloxypropyltrimethoxysilane (MPS), diphenyldimethoxysilane (DPhDMS), and zirconium isopropoxide (TPZ) with boric acid under anhydrous conditions. The methacryl groups of MPS are UV-polymerizable, which are suitable for low cost fabrication of waveguides with a UV write/develop process. The incorporation of DPhDMS and TPZ was found useful in reducing the optical loss and in enhancing the thermostability of the polymer. The refractive index of the hybrid polymer is tuneable from 1.4950 to 1.5360 by variation of the ratio among MPS, DPhDMS and TPZ. Optical characterisation showed that the material has low optical losses at the telecommunications windows (0.16 dB/cm at 1310 nm and 0.4 dB/cm at 1550nm). The hybrid polymer also showed a low birefringence (1.2 e-4), a large thermo-optic (TO) coefficiency (-3.0 e-4), and an outstanding linearity of dn/dT in a wide range of temperature (from 25°C to 200°C). Waveguides forming ability for the hybrid polymer with UV imprinting was also demonstrated.

11:45 AM Y4.12
INORGANIC-ORGANIC HYBRID MATERIALS FOR REAL 3D SUB-μm LITHOGRAPHY. R. Houbertz, J. Schulz, G. Domann, L. Fröhlich, and M. Popall, Institute for Silicate Research ISC, Würzburg, GERMANY; J. Serbin and B. Chichkov, Laser Center Hannover e.V. LZH, Hannover, GERMANY.

Real 3D sub-μm lithography was performed with two-photon polymerization (2PP) using inorganic-organic hybrid polymer (ORMOCER®) resins. The hybrid polymers were synthesized by hydrolysis/polycondensation reactions (sol-gel processing) which allows one to tailor their material properties towards the respective applications, i.e., dielectrics, optics or passivation.1 Due to their photosensitive organic functionalities, ORMOCER® can be patterned by conventional photo-lithography as well as by femto-second laser pulses. This results in polymerized (solid) structures where the

non-polymerized parts can easily be removed by standard developers. ORMOCER® structures as small as 200 nm or even below were generated by 2PP of the resins using femto-second laser pulses, where the laser is focussed into the volume of the resin. It is demonstrated for the first time, that ORMOCER® have the potential to be used in components or devices build up by nm-scale structures such as, e.g., photonic crystals.2 Aspects of the materials in conjunction to the applied technology are discussed. 1 M. Popall, A. Dabek, M.E. Robertsson, S. Valizadeh, O.J. Hagel, R. Buestrich, R. Nagel, L. Cergel, D. Lambert, and M. Schaub, Mol. Cryst. And Liq. Cryst. 354, 123 (2000).
2 J. Serbin, A. Egbert, A. Ostendorf, B. Chichkov, R. Houbertz, G. Domann, J. Schulz, L. Fröhlich, and M. Popall, Opt. Lett. (submitted). ®registered trademark of the Fraunhofer-Gesellschaft für Angewandte Forschung e.V.

SESSION Y5: PHOTONIC PROCESSING
Chairs: Ioanna Zergioti and Heungsoo Kim
Wednesday Afternoon, April 23, 2003
Olympic (Argent)

1:30 PM *Y5.1
TEMPORAL PULSE SHAPING AND OPTIMIZATION IN ULTRAFAST LASER ABLATION OF MATERIALS. Razvan Stoian, Sebastian Winkler, Matthias Hildebrand, Mark Boyle, Andreas Thoss, Arkadi Rosenfeld, and Ingolf V. Hertel Max-Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, GERMANY.

The necessity for enhanced controllability has promoted femtosecond technology to the forefront of material processing. In this respect ultrafast lasers offer unrivaled capabilities for reduced-scale processing, taking advantage of the nonlinear and selective interactions, reduced heat effects, and the unique possibility of pulse adaptive manipulation. Dielectric materials show specific ways to respond to the sudden laser energy input, depending on the efficiency of electron generation and on the ability to release the energy into the lattice. Electronic loss mechanisms, the efficiency of surface charging, as well as the strength of the electron-phonon interaction control the effectiveness of the energy deposition into the lattice. The developments in the field of dynamic pulse temporal tailoring and adaptive optimization introduce the possibility to regulate and manipulate excitation and energy transfer, to exploit dynamic processes and optimize structuring, unfolding new perspectives for "intelligent", feedback-assisted processing of materials. Effects of a modulated excitation on materials with different electronic relaxation times irradiated with temporally tailored pulses derived from time-resolved measurements of the ablation products and surface topology investigations will be presented. Smaller and controllable structures were achieved for materials with fast carrier trapping by applying pulses modulated on the time scale of the electronic decay. As a consequence of the accumulated mechanical stress, femtosecond laser micromachining of brittle dielectrics often results in specific collateral damage in forms of fracture and exfoliation. However, improvements can be made when temporally modulated pulses are used on materials exhibiting strong electron-lattice interactions. Carrier self-trapping induces local lattice deformations, softening the interaction region, and the use of modulated pulses determines an optimum energy deposition rate. It will be shown that the use of sub-ps modulated pulses enlarges the processing window and allows the application of higher fluences and number of sequences per site while keeping fracturing at a reduced level.

2:00 PM Y5.2
LASER ASSISTED MOLECULAR BEAM DEPOSITION (LAMBD). James F. Garvey, Dept. of Chemistry, University of Buffalo, State University of New York, Buffalo, NY; Robert L. DeLeon and Gary S. Tompa, AMBP Tech Corporation, Amherst, NY.

The Laser Assisted Molecular Beam Deposition process is related to conventional Pulsed Laser Deposition (PLD). In the PLD process, the ablation plume impinges directly upon the substrate to deposit the thin film, whereas in the LAMBD process, the ablation plume is directed within a concurrently pulsed stream of a carrier gas. The carrier gas pulse serves to transport (and cool) the ablated material to the substrate for deposition of the thin film. One advantage of the LAMBD process is that a chemically reactive carrier gas can be selected to produce desired chemical products (metal oxides, metal nitrides, metal carbides). By inject the reagent gas into the ablation plume of the metal target, novel molecular species can be generated. By controlling the molecular beam expansion, we are capable of "spraying" clusters onto a particular substrate which then coalesce to generate a uniform coating. Subtle modifications of laser fluence or expansion conditions result in dramatic changes in the chemical properties and morphology of the film generated For example, depositions on silicon and patterned silicon substrates yielded 5 nm to 100 nm of stoichiometric HfO2, and ZrO2 films, again employing the appropriate metal target and oxygen gas. A wide variety of other applications will be demonstrated (i.e, superconducting films, polymeric films, metal oxide:organic dye matrices, photonic devices, nanopowders, etc...).

2:15 PM Y5.3
PIEZOELECTRIC NEODYMIUM TITANATE NANOCERAMICS PRODUCED BY NOVEL SPARK-PLASMA-SINTERING TECHNIQUE. Guo-Dong Zhan, Department of Chemical Engineering and Materials Science, University of California, Davis, CA; Michael J. Reece, Department of Materials, Queen Mary University of London, UNITED KINGDOM; Joshua D. Kuntz and Amiya K. Mukherjee, Department of Chemical Engineering and Materials Science, University of California, Davis, CA.

Neodymium titanate is a member of a family of ferroelectric materials with a perovskite-type layered structure. It has found that single crystals of neodymium titanate exhibited piezoelectric and electro-optic properties and had a high positive temperature coefficient of capacitance along with an extremely high Curie temperature of 1773 K. These characteristics have made them very promising as high temperature ferroelectrics for use in high temperature devices as well as being potentially useful for dielectrics and resonators at ambient temperature. Spark-plasma-sintering (SPS) is a new process by which ceramics can be consolidated very rapidly to full density. In the present study, this novel SPS technique has been applied to produce neodymium titanate nanoceramics with improved properties. Fully dense neodymium titanate materials could be consolidated by SPS at relatively low temperatures for just a few of minutes. The sintering conditions including heating rates, microstructural development, and resultant properties have been investigated. The dielectric measurements were made using a precision impedance analyzer at various frequencies between 50 Hz and 1 MHz. The electrical field-induced polarization was measured at room temperature using a Swayer-Tower circuit at 1Hz, and the polarization and the coercive field were determined from the polarization-electrical field (P-E) hysteresis loops.

2:30 PM Y5.4
MICRON-SCALE BUCKLING OF SiO_2 ON Si. Justin R. Serrano and David G. Cahill, University of Illinois at Urbana-Champaign, Dept of Materials Science and Engineering and the Fredrick Seitz Materials Research Laboratory, Urbana, IL.

Surface texturing with nanosecond laser pulses provides a method for creating novel modifications to surface morphology. By using compressively strained SiO_2 films on silicon, we are able to obtain highly ordered periodic surface structures after laser melting of the silicon substrate. The compressive stress in the films leads to elastic buckling and, with the constraint of a liquid substrate, produces the periodic morphology. Unlike other laser texturing procedures that rely on hydrodynamic flow driven by temperature gradients, the resulting surface structure does not exhibit a strong dependence on laser energy. Instead, the wavelength λ of the buckled surface scales with the film thickness, $\lambda = h_f/\sqrt{8\epsilon(1+\nu)}$, and its amplitude saturates at $A = h_f/\sqrt{6}$, where h_f, ϵ, and ν are the thickness, residual strain, and Poisson's ratio of the film. For 50 nm SiO_2 films, the experimental wavelength of 1.6 μm and amplitude of $\sim$18 μm are in good agreement with theory. For melt diameters smaller than 3 μm, the films undergo a downward central deflection—similar to buckling of clamped circular plates—but, because of volume conservation of the liquid underneath, also suffer an upward deflection at the melt edges. At laser fluences near the ablation threshold of the substrate, homogeneous nucleation of a void at the SiO_2/Si interface leads to delamination of the film from the substrate and subsequent buckling away from the interface.

2:45 PM Y5.5
ULTRAVIOLET RADIATION ASSISTED OXIDATION OF PULSED LASER DEPOSITED HALFNIUM METAL FILMS ON SILICON FOR ALTERNATE HIGH-k GATE DIELECTRICS. C. Essary, J.M. Howard, V. Craciun, and R.K. Singh, Dept of Materials Science and Engineering, University of Florida, Gainesville, FL.

Currently in the search for an alternate high-k dielectric material to replace silicon dioxide, halfnium oxide has shown promise due to the thermodynamic stability on silicon and higher dielectric constant. However, a low temperature deposition method is necessary to limit possible reactions with the silicon. Use of ultraviolet radiation can aid in the oxidation of the metal and provide better interfaces at lower temperatures and lower oxygen pressures. In this study, thin films of halfnium metal ranging from 5-50 nm have been deposited on silicon wafers using a conventional pulsed-laser system. The films were then heated and oxidized in an oxygen rich atmosphere. A set was oxidized in the presence of an array of mercury vapor lamps emitting radiation

in the 185 and 254 nm wavelength regions, and another set was oxidized in the presence of a xenon excimer lamp radiating at 172 nm. Film quality and stoichiometry was assessed using x-ray photospectroscopy, x-ray reflectivity, and fourier transform infrared spectroscopy. Electrical properties of the films were compared using capacitance-voltage and current-voltage measurements with platinum electrodes and a comparison between the ultraviolet, excimer, and non-irradiated samples were made. High-resolution transmission electron microscopy was used to examine the interfacial differences in the films in order to tie the findings of the electrical characterization to the structure of the film.

3:15 PM Y5.6
SYNTHESIS OF DILUTED SEMICONDUCTOR ALLOYS BY ION IMPLANTATION AND PULSED LASER MELTING.
O.D. Dubon[a,b], M.A. Scarpulla[a,b], K.M. Yu*b*, W. Walukiewicz[b], O. Monteiro[b]; [a]Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, CA; [b]Lawrence Berkeley National Laboratory, Berkeley, CA.

Alloying is a well-established method used to tailor the electrical and optical properties of semiconductors. Control over the energy band gap of a material, or so-called band gap engineering, lies at the heart of today's most advanced quantum-well devices. In many alloy systems, producing the needed changes in properties requires modifications in composition with the alloying species well beyond several atomic percent for which advanced thin-film deposition techniques are necessary. However, recently a novel class of semiconductors has emerged, whose fundamental properties are dramatically modified through the substitution of a relatively small fraction of host atoms with a very different element. Among these diluted alloys are GaN_xAs_{1-x}, which exhibits a reduction of the band gap by as much as 180 meV per x=0.01, and $Ga_{1-x}Mn_xAs$, which displays ferromagnetic behavior for x<0.1. Here we demonstrate the synthesis of these materials by a combination of ion implantation and pulsed laser melting. GaN_xAs_{1-x} produced using this method followed by rapid thermal annealing exhibits a fundamental band gap of 1.26eV (a band gap reduction of 160meV compared to GaAs) for x=0.018. In contrast to synthesis by N ion implantation and rapid thermal annealing only, the introduction of pulsed laser melting improves N incorporation in the films by a factor of five. $Ga_{1-x}Mn_xAs$ films formed by Mn ion implantation into GaAs and subsequent pulsed laser melting are single crystalline with a Mn substitutional fraction as high as 80% for x=0.03 and a remnant magnetization persisting above liquid nitrogen temperatures for samples with x=0.10 and a substitutional fraction of 40%. This versatile approach for the synthesis of diluted semiconductor alloys opens exciting opportunities for the study of a wide range of materials systems. We discuss these results as well as the prospects for the realization of device heterostructures.

3:30 PM *Y5.7
OPTICAL PHONON STUDY NEAR SUB-PICOSECOND FUSION THRESHOLD.
A. Rousse[a], D. Boschetto[a], C. Rischel[b], O. Albert[a], I. Uschmann[c], S. Fourmaux[a], D. Hulin[a], E. Förster[c], and J. Etchepare[a]. [a]Laboratoire d'Optique Appliquée, ENSTA/Ecole Polytechnique, UMR 7639 CNRS, Chemin de la Hunière, Palaiseau, FRANCE; [b]Niels Bohr Institute, Copenhagen, DENMARK; [c]X-ray Optics Group, Institute of Optics and Quantum Electronics, Friedrich Schiller University Jena, Jena, GERMANY.

The sub-picosecond time scale is of capital importance in studying dynamical evolution in the matter, as it represents the firsts instants of the material response to the external excitation. When such dynamics can be triggered by an ultra-short laser pulse, a pump-probe experiment allow the measurement of transient state during the induced transition in the material. In this category, a very exciting class of phase transition is the sub-picosecond fusion induced by an intense and ultra-short (100 femtosecond) laser pulse. This mechanism is often called non-thermal melting since the transition takes place on a time scale much shorter then the time required to transfer the energy from the excited electrons to the thermal motion of the lattice. Instead, optical phonons could drive this phase transition, as they are generated on a time scale comparable or even less than the duration of the laser-induced melting. The new emerging tool of femtosecond X-ray diffraction [1] allowed already a direct monitoring of the atomic position during such a phase transition [2] following the change in time of one Bragg peak after the excitation pulse. In this paper we show some measurement of coherent optical A_{1g} phonon near the fusion threshold in case of Bismuth material, as bulk and as thin film. This mode is efficiently excited by a 100 femtosecond laser pulse via displacive mechanism. The behavior of atomic displacements is directly measured by the perturbation of the X-ray diffraction signal, because of the change in the structure factor. Modification of the characteristic parameters of the optical phonons (frequency, amplitude, dumping time) near the phase transition will give some additional information on the contribution of the selected normal mode to the whole dynamics. [1] C. Rischel et al., Nature 390, 490 (1997). [2] A. Rousse et. al, Nature 410, 65 (2001).

4:00 PM Y5.8
PULSED LASER PROCESSING OF METALS AND SEMICONDUCTORS IN REACTIVE ATMOSPHERES: LASER NITRIDING AND CARBURAZING.
Ettore Carpene and Peter Schaaf II, Physikalisches Institut, Universität Göttingen, GERMANY.

Hard surface coatings and thin layers can be synthesized by irradiating pure substrates with short laser pulses in reactive atmospheres. Various lasers with different pulse durations τ and wavelengths λ can be used for this purpose: XeCl Excimer Laser (τ=55 ns, λ=308 nm), Nd-YAG Laser (τ=8 ns, λ=1060 nm), Free Electron Laser (τ=2 ps, λ=3.1 μm) and Ti:Sapphire-Laser (τ=150 fs, λ=750 nm) [1]. The irradiation of materials such as aluminum, iron, titanium and silicon in controlled nitrogen and methane atmospheres leads to surface modifications (e.g. hardness improvement) and to the formation of homogeneous coatings. The evolution of the surface properties (phase formation, hardness) as well as the mass transport mechanism during the laser irradiation have been studied in detail as a function of the experimental parameters (laser fluence, ambient gas pressure, number of laser shots) for the Excimer Laser treatments [2-5]. The formation of homogeneous AlN layers after irradiation of aluminum substrates in N_2 atmosphere, the synthesis of homogeneous cementite coatings after irradiation of iron substrates in CH_4 atmosphere and the successful incorporation of carbon after irradiation of (100) and (111) silicon single crystals in methane gas will be reported. [1] P. Schaaf, M. Han, K.P. Lieb, E. Carpene, Appl. Phys. Lett. **80** (2002) 1091. [2] E. Carpene and P. Schaaf, Phys. Rev. B **65** (2002) 224111. [3] E. Carpene and P. Schaaf, Appl. Phys. Lett. **80** (2002) 891. [4] E. Carpene, A.M. Flank, A. Traverse and P. Schaaf, J. Phys. D: Appl. Phys. **35** (2002) 1428. [5] P. Schaaf, Progr. Mater. Sci. **47** (2002) 1.

4:15 PM Y5.9
WAVELENGTH DEPENDENCE OF UV-LASER INDUCED EMISSION OF NEUTRAL AND IONIC SPECIES FROM SINGLE CRYSTAL IONIC MATERIALS.
Loren Cramer, Steve Langford, Tom Dickinson Washington State University, Pullman, WA; Wayne Hess, Pacific Northwest National Laboratory, Richland, WA.

An investigation into photo-induced material breakdown is reported using time-resolved, quadrupole mass-selected measurements of neutral and ion emission from single crystal ionic materials with ns-pulsed excimer lasers at wavelengths of 157 nm, 193 nm, 248 nm and 308 nm. Studies on CaF_2 (transmittance down to 157 nm is greater than 80%) have shown ionic desorbing species include Ca^+ and CaF^+ during 157 nm irradiation and Ca^+ for all other wavelengths. Electron irradiated surfaces become metal enriched and should show increased Ca^+ ion emission. CaF_2 forms nano clusters of Ca on and near the surface of electron irradiated surface which absorbs at greater than 300 nm, so the effects on the shorter wavelengths have not been studiesd. For $NaNO_3$ (Does not transmit UV), neutral species, including NO, O_2, N_2, and Na are observed at all three wavelengths. At 193 nm, intense atomic N and O emissions are also observed, possibly due to a 1+1 excitation involving the π^* <-π transition in the nitrate ion (centered at 6 eV) followed by excitation to a higher excited state. This transition is not efficiently excited at the other wavelengths. Although 157 nm photons do not excite the π^* <-π transition efficiently, the resulting NO emission is found to be quite intense: on a per photon basis, 157-nm photons are much more efficient in decomposing nitrate anions than 193-nm photons. Intense ion emission (principally Na^+ and NO^+) is observed at 193 and 157 nm, with weaker Na^+ emission at 248 nm. The ion intensities show high-order fluence dependence, consistent with photoelectronic emission involving sequential photon absorption as described earlier for 248-nm irradiation. Electron irradiated $NaNO_3$ surfaces show a metal enriched surface that allows for a more uniform pulse to pulse desorption of Na^+ ions.

4:30 PM Y5.10
DIRECT PHOTO-IMPRINTING IN HIGH PHOTOSENSITIVE ORGANICALLY MODIFIED GERMANOSILICATE GLASSES.
Jae Hyeok Jang, Dong Jun Kang and Byeong-Soo Bae, KAIST, Dept of Materials Science and Engineering, Daejeon, REP. OF KOREA.

Germanium doped silica glasses have received much attention because of the ultraviolet-induced refractive index change. In this case, refractive index changes through defect reaction within the glass, but surface relief grating is rarely found. Here we report on the inscription of both surface relief pattern and refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass using its large volume change induced by ultraviolet exposure. The refractive index change, density change, structural variations and microstructure of the ORMOGSIL glasses with the UV irradiation were investigated. A large refractive index increase up to 10^{-2} is induced by ultraviolet-induced densification in the ORMOGSIL glasses. Density

increased linearly with the UV fluence same as refractive index change behavior. Calculated refractive index change through Lorentz-Lorenz equation was about 10^{-2}, which is in good agreement with the experimental data. The shifts in frequency of the Raman bands confirm that, for ORMOGSIL glasses, structural densification by reduction of the average intertetrahedral (Si-O-Si) bonding angle in silica network accounts for a major part of the photosensitive effect. Also, a surface AFM scans of unetched sample show that the volume compaction in the ultraviolet illuminated region is associated with periodic pattern inscription. This presents direct evidence for the photoinduced densification in ORMOGSIL glasses. Although the writing time for the periodic refractive index modulation is relatively slow, this large index change and the direct inscription of relief pattern in ORMOGSIL glasses have allowed the easy development of grating based devices that have wide range of optical device applications.