SYMPOSIUM G

Luminescence and Luminescent Materials

April 17 – 19, 2001

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* Invited paper

SESSION G1: THEORY, MODELING & LUMINESCENCE PHENOMENA
Chair: B. DiBartolo
Tuesday Morning, April 17, 2001
Franciscan II (Argent)

8:30 AM *G1.1
QUANTUM CASCADE LASERS; A "UNIVERSAL" LIGHT SOURCE FOR THE ENTIRE INFRARED SPECTRUM.
Federico Capasso, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Quantum cascade lasers (QCL) are fundamentally new in that: (1) their wavelength can be tailored over a wide range (so far from 3.4 μm to 20 μm and in the future from 1 to 100 μm and beyond) using the same combination of materials by a suitable choice of the active layer thicknesses (a few μm), (2) their optical power is greatly enhanced by the cascade effect (one injected electron creates 25-75 photons in traversing the active region). These devices invented at Bell Labs in 1994, now outperform all other mid-ir semiconductor lasers in peak and cw optical power (0.5 W at 300 K and 0.2 W at 80 K with maximum operating temperatures of 175 K, in pulsed and cw mode respectively), and single mode tunability with >30 dB side mode suppression ratio(up 150 μm).[1,2] This talk will discuss in a simple way the underlying device physics, design principles and performance of our state-of-the-art top-of-line QCLs used in scientific, commercial and military application as well as exciting recent results such as multi-wavelength and bi-directional QCLs, surface plasmon QCLs for the far infrared, ultra-high-speed gain-switched and modelocked QCLs. Results of spectroscopic applications of distributed feedback QCLs to high resolution atmospheric chemistry, trace gas analysis and to point sensors/LIDAR for environmental monitoring will be discussed. QCLs have been used by our collaborators to detect trace gases (e.g. nitrous oxide, NO, ammonia, methane and its isotopes, ethanol, etc.) in the open atmosphere and in a cell in the range from $\sim$ one part per million in volume to less than a part per billion, with techniques such direct absorption and wavelength modulation spectroscopy, photoacustic and cavity ring-down spectroscopy. Free running cw QCLs have linewidths of a few MHz, while with appropriate side-locking stabilization linewidths down to 10 KHz have been demonstrated.[3] This research is in part supported by DARPA/ARO under contract DAAG55-98-C-0050. 1. F. Capasso et. al. Optics and Photonics News, 10, pp. 31-37, October 1999; Physics World, 12, pp. 27-33, June 1999. 2. http://www.bell-labs.com/org/physicalsciences/projects/qcl/qcl.html;http://www.bell-labs.com/org/physicalsciences/psr/qc/index.html 3. R.M. Williams et al. Optics Letters 24, pp 1844-1846, 1999 (Dec. 15)

9:00 AM G1.2
A FIRST-PRINCIPLES STUDY OF HOST EXCITATION IN GALLATES.
K.C. Mishra, Central Research, OSRAM Sylvania Inc., Beverly, MA; V. Eyert, Institut für Physik, Universität Augsburg, Augsburg, , GERMANY; J. Sticht and P.C. Schmidt, Dept. of Physical Chemistry, TU-Darmstadt, GERMANY.

Using density functional ab initio methods (augmented spherical waves and full potential linear muffin-tin orbitals), we investigate common trends in the optical transitions in gallates and the corresponding binary oxides. We report the electronic structures of three gallates, monoclinic and orthorhombic $CaGa_2O_4$ and the partially inverted spinel $MgGa_2O_4$ and the corresponding binary oxides CaO, MgO and α- and β- Ga_2O_3. The main objective of this investigation is to explore how the electronic structures of ternary oxides relate to their binary oxides and to analyse the nature of electronic processes when the optical excitation involves the host lattice. In the binary oxides CaO, MgO and Ga_2O_3, the optical gap is determined by electronic transitions from almost pure 2p-like states of oxygen to the metallic states near the conduction band minimum. The metallic states near the bottom the conduction band vary from pure s-like states in MgO and Ga_2O_3 to hybrid states with s- and d-like character in CaO. The bandwidths of the 2p-like bands of oxygen are about 3 eV in CaO, 4 eV in α- Ga_2O_3 and 5 eV in MgO whereas in β-Ga_2O_3 this bandwidth is larger by a factor two. The increase in bandwidth in β- Ga_2O_3 is mainly due to its complex crystal structure and larger covalent contributions to the chemical bonds. Increasing covalency in β-Ga_2O_3 leads to a smaller optical gap in this material compared to those of CaO, α-Ga_2O_3 and MgO. The ordering of the electronic states for the ternary oxides $CaGa_2O_4$ and $MgGa_2O_4$ can be interpreted qualitatively as a superposition of the electronic states of the corresponding binary oxides. A detailed analysis of the band structures of these oxides will be discussed in the context of optical excitations near the band edge.

9:15 AM G1.3
ENERGY TRANSFER AND RELAXATION IN LUMINESCENT MATERIALS USED AS PHOSPHORS.
David R. Tallant, Carleton H. Seager and Regina L. Simpson, Sandia National Laboratories, Albuquerque, NM.

The relaxation of excited states in light-emitting atoms (activators) present at doping levels (a few tenths up to ten atom percent) in crystalline hosts involves photon and phonon emission, energy transfer and migration of excited state quanta. The complex interplay of these interactions has made it difficult to identify specific mechanisms limiting emission efficiency in these materials. In applications where these materials are used as phosphors, such as computer monitors and other types of displays, low emission efficiency impacts the performance of the display device. We have investigated relaxation mechanisms in a number of diverse systems employed as phosphors and have found a common mechanism which significantly limits emission efficiency. This mechanism involves an energy transfer interaction between excited activators which effectively dissipates, as phonons, one of the two excited state quanta, both of which would otherwise be emitted as photons. We have found evidence for this interaction in the following systems: yttrium oxide: europium, yttrium silicate: terbium, zinc silicate: manganese and strontium thiogallate: europium. We will present evidence for these interactions in the form of photo- and cathodoluminescence persistence curves of emission as a function of excited state energy, activator concentration and excitation intensity. We will show how modeling of the emission behavior of these systems requires the consideration of second-order kinetic effects from excited activator interactions and diffusion effects from the migration of excited state quanta between activators, as well as first-order relaxation phenomena (photon and phonon emission). We will also present results from emission experiments at cryogenic temperatures, which separate phonon-dependent interactions from those which do not involve phonons and provide insight into the nature of the activator interaction mechanism.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

9:30 AM G1.4
ELECTRIC FIELD INSIDE A COATED ELECTROLUMINESCENT PARTICLE EMBEDDED IN A DIELECTRIC MEDIUM CONTAINING MANY SIMILAR PARTICLES.
K.C. Mishra, Richard C. Garner, OSRAM Sylvania, Light Sources Research, Beverly, MA.

The brightness of an electroluminscent particle depends critically on its internal electric field, which induces electrons to acquire enough kinetic energy to excite activator ions. Typically, an electroluminescent device consists of a collection of electroluminescent particles embedded in dielectric medium. To prevent adsorption of water and other contaminants, the particles are coated with a protective layer. In this work we have calculated the electric field internal to the particles of such a composite system and have studied the effects of the values of the dielectric constants, the coating and particle diameters, and the volume fraction of particles contained in the system on the field.
The internal electric field in a system of non-coated particles was investigated previously by Roberts (*J Opt Soc Am*, 42(11), 850-854, 1952). We have extended the approach to a system containing coated particles. The internal electric field is calculated first for a single coated (speherical) dielectric particle embedded in an infinite dielectric medium in which there is a uniform applied electric field. The internal field is simply the solution to the Laplace equation with the appropriate boundary conditions at the interfaces of the particle and coating and of the coating and surrounding material.
To account for the presence of the other particles the applied electric field in the single particle calculation is replaced by the local electric field, which is the applied field modified by the dipolar field of all the other particles. Using the Clausius-Mosotti equation, the local field is related to the applied field, the particle density, and particle polarizability. The polarizability is obtained directly from the single particle calculation. The result is self-consistent expression for the internal field in terms of the applied field, the particle density and material properties.
The Clausius-Mosotti equation further provides the effective dielectric constant of the composite system. This is a directly measurable quantity and can be used to extract the dielectric constant of the coating or, alternatively, of the particles.

10:15 AM G1.5
UPCONVERSION STUDIES OF Lu_2O_3:Er^3.
J.A. Capobianco, F. Vetrone, J.C. Boyer, Concordia University, Department of Chemistry and Biochemistry, Montreal, CANADA; M. Bettinelli, A. Speghini, Università di Verona, Dipartimento Scientifico e Tecnologico, Verona, ITALY.

Over the years, there has been considerable attention focused on the phenomenon of upconversion. Upconversion refers to the optical illumination of an ion-doped material, which produces population in an excited state whose energy exceeds that of the pump photon.

Presently, a large amount of interest has been focused on a new class of systems with restricted geometry; rare earth doped nanocrystalline particles whose dimensions range from sub-nanometers to several tens of nanometers. This interest in nanocrystals is fueled by their potential as efficient display phosphors in opto-electronic applications as a result of their enhanced optical properties. In this paper, we investigate the upconversion properties of nanocrystalline and bulk Lu_2O_3 doped with 1 mol% Er^{3+}. The Er^{3+} doped Lu_2O_3 nanocrystals were synthesized using the solution combustion method starting from an aqueous solution containing glycine, $Lu(NO_3)_3 \bullet 6H_2O$ and $Er(NO_3)_3 \bullet 6H_2O$, yielding nanoparticles with a size of about 50 nm. For comparison purposes a bulk sample was prepared by mixing Lu_2O_3 and Er_2O_3 and pressing the powders into a pellet under 10 tons of pressure and firing at 1500°C for 24 hours. Continuous wave excitation (804 nm) of the bulk and nanocrystalline samples into the $^4I_{9/2} \leftarrow {}^4I_{15/2}$ transition produced intense luminescence spectra. The observed bands are assigned to the following transitions; $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition centered at 530 nm, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition centered at 555 nm and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition centered at 665 nm. The possible mechanism for populating the $^2H_{11/2}$ and $^4S_{3/2}$ states involves bringing the Er^{3+} ions into the $^4I_{9/2}$ level using 804 nm laser radiation. Following this, a non-radiative relaxation occurs which brings the Er^{3+} ions down to the $^4I_{11/2}$ level. Finally, energy transfer occurs via the following mechanism, $2\ {}^4I_{11/2} \rightarrow {}^4I_{15/2} + {}^4F_{3/2}$. Relaxation feeds the $^4S_{3/2}$ level and thermalization populates the $^2H_{11/2}$ level. A brief comparison of the upconversion spectra of Lu_2O_3:Er^{3+} to those of Y_2O_3:Er^{3+} is also presented.

10:30 AM G1.6
ADVANCES IN THE DEVELOPMENT OF QUANTUM SPLITTING PHOSPHORS. A.A. Setlur, A.M. Srivastava, GE Corporate Research and Development.

Current phosphors are able to convert (at best) one VUV photon into one visible photon. The development of quantum splitting phosphors (QSPs) with a visible quantum efficiency greater than unity for VUV excitation would minimize the Stokes shift energy losses. This could lead to significant improvements in the efficiency of Hg and Xe based low-pressure discharge lamps. In this talk, we will describe the recent developments pertaining to different schemes for QSPs such as Pr^{3+} doped hosts, energy transfer between Gd^{3+} and Eu^{3+}, and energy transfer between Er^{3+}, Gd^{3+}, and Tb^{3+}. The applicability of these schemes to current fluorescent lamp products will be analyzed. In addition, we will be specifically discussing our results for Pr^{3+} based QSPs. Using measured Judd-Ofelt parameters and theoretical considerations, we are able to determine maximum quantum efficiencies for Pr^{3+} QSPs. In addition, we have determined the onset of concentration quenching and other non-radiative decay paths in these phosphors. This gives us a guide to optimize the composition of Pr^{3+} QSPs. The potential use of these phosphors in low pressure Hg discharge lamps will also be discussed.

10:45 AM G1.7
DEVELOPMENT OF A DYE SOLUTION FOR OPTICAL COOLING BY ANTI-STOKES FLUORESCENCE.
Jarett Bartholomew, University of California, Dept of Chemical and Materials Physics, Irvine, CA; Peter DeBarber, Bauke Heeg, MetroLaser, Inc. Irvine, CA; Garry Rumbles, National Renewable Energy Lab, Golden, CO.

Optical cooling by means of anti-Stokes luminescence in condensed media has been observed by several independent groups. The most promising materials are grouped into two categories: ion-doped glasses and organic dye solutions. It is this latter group that we focus our efforts on. The dye solutions exhibit several important properties necessary for the development of an optical refrigerator including: near unit quantum yield, short fluorescence lifetime, large Stokes loss factor, large choice of excitation/pump wavelengths, and low cost. Recent studies by our group show that irradiating a solution of rhodamine 101 in the long wavelength wing of the absorption spectrum results in the observation of optical cooling. To improve upon the initial observation of a few degrees drop in temperature requires a better understanding of the conditions and phenomena leading to anti-Stokes luminescence in dye solutions. In this presentation, we discuss our experiments designed to study and optimize the dye solution and conditions for optical cooling including quantitative quantum yield measurements by thermal lensing. The importance of deuteration, acidification, concentration, pump wavelength, and optical geometry are considered and discussed. The results from the optimized dye solution experiments are placed in context to the overall objective of developing an all-optical refrigerator.

11:00 AM G1.8
COMPUTER MODELLING OF LUMINESCENCE IN ABO_3 PEROVSKITES. R.I. Eglitis[a], E.A. Kotomin[a,b] and G. Borstel[a], [a]Dept. of Physics, University of Osnabrueck, Osnabrueck, GERMANY; [b]Institute of Solid State Physics, University of Latvia, Riga, LATVIA.

Many ABO_3 ferroelectric perovskites reveal a photoluminescence in the visible range ('green luminescence' peaking around 2.2 eV in $KTaO_3$ and $KNbO_3$). There were many hypothetical mechanisms suggested as an origin of this luminescence including donor-acceptor recombination, recombination of electron and hole polarons, charge transfer vibronic excitation (CTVE), electron transitions in MeO_6 complexes, etc. We performed quantum chemicall modelling of the atomic and electronic structure of the triplet excitons in $KNbO_3$ and $KTaO_3$ and calculated their luminescence energies. Our calculations give a strong support to the 'green' luminescence in $KTaO_3$ and $KNbO_3$ crystals as a result of the recombination of the electrons and holes forming the charge transfer vibronic exciton rather than due to the electron transitions in MeO_6 complex. The luminescence energy calculated using the ΔSCF method in both $KTaO_3$ and $KNbO_3$ is very close to the experimentally observed 2.2 eV.

SESSION G2: CHARACTERIZATION
Chair: David R. Tallant
Tuesday Afternoon, April 17, 2001
Franciscan II (Argent)

1:30 PM *G2.1
ANALYSIS OF TUNGSTATES AND SESQUIOXIDES,TWO OF THE BEST Yb^3 -DOPED LASER CRYSTALS ACCORDING TO DIFFERENT EVALUATIONS. Georges Boulon, Alain Brenier, Laetitia Laversenne, Yannick Guyot, Marie-Thérése Cohen-Adad, Gérard Métrat, Noelle Muhlstein, LYON 1 Univ, Dept of Physics and Chemistry of Luminescent Materials, Villeurbanne, FRANCE.

The development of reliable InGaAs laser diode pump sources emitting in the 900-980 nm spectral range is stongly influencing the field of lasers based on Yb^{3+}-doped solid state crystals. The Yb^{3+} ion have some advantages over the Nd^{3+} ion as laser emitting center due to its very simple energy level scheme, constituted of only two levels: the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state. Among new directed searches for novel laser crystals, one important is the use of Yb^{3+} active ion in an inertial-fusion-energy diode pumped solid state laser. $Ca_5PO_4$3F {C-FAP} and S-FAP {S=Sr} were soon recognized to be favourable hosts for Yb^{3+} lasing. This fact was supported by an evaluation of the spectroscopic properties of several Yb^{3+}-doped crystals useful for laser action[1]. This evaluation is based on two parameters known from spectroscopy, the emission cross-section at the laser wavelength and the minimum pump intensity required to achieve transparency at the laser wavelength. In the diagram, C-FAP and S-FAP appear to be exceptionally good, and YAB $\{YAl_3\{BO_3\}4\}$,GdCOB $\{CaGd_4\{BO_3\}3O\}$or YAG appear modest. This is somewhat in contradiction with experimental laser tests in which these latter materials are revealed very efficient. According to another evaluation [2-3],we present here the main spectroscopic properties of two of the best Yb^{3+}-doped laser crystals,which are grown in our Group: (i) tungstates by the Floating Crystal method [4] and (ii) sesquioxides by the Laser Heated Pedestal Growth method [5]. Such an evaluation, based on a quasi-three level laser model, leads to compare all known Yb^{3+}-doped crystals in a two-dimensional diagram considering the laser extracted power and the slope efficiency. We shall show that both, tungstates as $KY\{WO_4\}2$ and sesquioxides as Sc_2O_3, have the highest laser potential. [1] D. DeLoach, S.A. Payne, L.L. Chase, L.K. Smith, W.L. Kway, W.F. Krupke, IEEE J. Quant. Electr. Vol. 29 no 4 (1993) 1179 [2] A. Brenier, J. of Luminescence (in press) [3] A. Brenier, G. Boulon, J. of Alloys and Compounds (accepted September 2000) [4] G. Métrat, M. Boudeulle, N. Muhlstein, A. Brenier, G. Boulon, J. of Crystal Growth 197 (1999) 883 [5] L. Laversenne, Y. Guyot, C. Goutaudier, M.T. Cohen-Adad, G. Boulon, Optical Materials (accepted April 2000)

2:00 PM G2.2
OBSERVATION OF CROSS-IONIZATION IN GSAG:Ce^{3+}.
Uwe Happek, Jongwoo Choi, Dept. of Physics and Astronomy, The University of Georgia, Athens, GA; Daniel Doxsee, GELcore, Independence, OH; Alok Srivastava, GE Corporate Research and Development, Niskayuna, NY.

The photoconductive spectrum of the garnet $Gd_3Sc_2Al_3O_{12}$:Ce^{3+} has been investigated. For the measurements, a single crystal (size $5 \times 4 \times 1$ mm^3) was mounted between two nickel meshes serving as transparent electrodes. Sapphire plates electrically insulated the electrodes from the copper coldfinger of a temperature variable cryostat.
Persistent photocurrents were excited with the radiation from a 300 W Xe arc lamp filtered through a f/2 double monochromator

(McPherson). Photocurrents as a function of excitation wavelength were recorded by a Keithley 6517 electrometer. Under an applied electric field of 10,000V/cm the observed current varied between 10^{-15} and 10^{-13}A, with a noise level below 10^{-15}A.
The obtained photoconductivity spectra reveal an ionization threshold of the Ce^{3+} ions at 3.4 eV, which allows to locate the Ce^{3+} energy levels relative to the host valence and conduction band. In addition, we find narrow peaks in the photoconductive spectrum around 4.0 eV and 4.5 eV, coinciding with f-f transitions of Gd ions. We attribute these peaks to cross-relaxation between Gd and Ce ions, leading to a promotion of the Ce^{3+} 4f electron into the conduction band. To our knowledge, these results are the first experimental evidence of a *cross-ionization* process. We will discuss results of experiments performed on other cerium doped garnets.

2:15 PM G2.3
DIRECT EVIDENCE OF FREE ELECTRON RELATED RECOMBINATION IN AN $In_{0.08}Ga_{0.92}N$ EPITAXIAL LAYER REVEALED BY MAGNETOLUMINESCENCE SPECTROSCOPY. Hiromitsu Kudo, Tomoyuki Tanabe, Hiroki Ishibashi, Ruisheng Zheng, Yoichi Yamada, Tsunemasa Taguchi, Yamaguchi Univ, Faculty of Engineering, Yamaguchi, JAPAN.

The radiative recombination mechanism in an $In_{0.08}Ga_{0.92}N$ epitaxial layer has been investigated by means of magnetic-field-dependent, and time-resolved photoluminescence (PL) measurements. Two emission components were clearly observed in the PL spectra with an energy separation of 40 meV. The decay time of the higher-energy component was almost constant of about 30 ps up to 300 K. On the other hand, the decay time of the lower-energy component decreased dramatically from 540 to 30 ps with increasing temperature from 6 to 160 K [1]. The carrier transfer between the two energy levels was clearly observed from the temperature dependence of luminescence intensities [2]. When magnetic field was applied in the Voigt configuration at 100 K, the two peaks indicated a linear energy shift (2.5 meV at 8 T) as a function of magnetic field, which is derived from the Landau energy shift of s-like electrons in the conduction band. This result gives direct evidence that the two energy levels originates from free carrier recombination when temperature is over 100 K. The intensity of the two peaks was increased with applied magnetic field, which is ascribed to the increased integration of the electron and hole wavefunctions by the magnetic field induced reduction of the dimensionality of the carriers. On the other hand, in the Faraday configuration, the shift of the two peaks was relatively small (about 1.5 meV at 8 T). Such a difference attributes to the anisotropic electron effective mass, which has been studied theoretically from the strong electron-phonon interaction approach. All these results can be explained by the two-energy-levels configurational coordinate model in the framework of strong electron-phonon interaction. The height of potential barrier between the two energy levels will also be discussed on the basis of our experimental evidence. [1] H. Kudo et al., J. Lumin. 87-89, 1199 (2000). [2] H. Kudo et al., Phys. Status Solidi A 180, 27 (2000).

2:30 PM G2.4
OPTICAL PROPERTIES OF RECRYSTALLIZED Ti:Al_2O_3 ON SAPPHIRE. J.F. Muth, Y.C. Chang J.C. Roberts, ECE Dept, NCSU, Raleigh, NC; H. Wang, A. Kvit, A.K. Sharma, J. Narayan, Dept. Mat. Sci. Eng., NCSU, Raleigh, NC.

Doped planer waveguides are an emerging photonic technology for the development of miniature compact lasers in the visible and near IR regions due to their compatibility with fiber and integrated optoelectronic devices. Titanium doped amorphous sapphire was deposited on crystalline sapphire substrates by Pulsed Laser Deposition. The amorphous material was then annealed in an oxygen ambient atmosphere to crystallize the amorphous layer and to optically activate the titanium. Rutherford backscattering/channeling was used to investigate the lattice perfection and the location of the Ti. High Resolution TEM was also used to verify that that resulting material was single crystal indicating that solid phase epitaxial growth occurred. Optical transmission and photoluminescence was used to determine that the titanium was optically activated. The index of refraction of the titanium-doped eptiaxial sapphire layer was higher than that of the undoped sapphire forming an optical waveguide. In some films sub micron voids were observed in High Resolution TEM which increased the scattering of light.

2:45 PM G2.5
HIGH PRESSURE LUMINESCENCE MEASUREMENTS ON Sm^{2+}-DOPED SOL-GEL GLASSES. Vilma C. Costa, Yongrong Shen, Kevin L. Bray, Dept of Chemistry, Washington State University, Pullman, WA; Ana M.M. Santos, Center of Nuclear Technology Development/CNEN, Pampulha, Belo Horizonte, MG, BRAZIL.

Samarium(II) doped crystals and glasses have attracted much attention for potential applications in lasers, fiber amplifiers and memory devices. Sm^{2+} has a ground $4f^6$ configuration and an excited $4f^5 5d$ configuration. The close proximity of the two configurations leads to a mixing of the states from the two configurations and to an alteration of the optical properties of Sm^{2+}. With high pressure we can tune the extent of mixing of the two configurations by varying their energy separation. As a result, we can systematically investigate how the extent of mixing varies the static and dynamic emission properties of Sm^{2+} and correlate the emission properties with with crystal field strength and coordination environment. Glasses containing 2, 5, and 10 wt% Sm_2O_3 in the systems Na_2O-Al_2O_3-SiO_2 and Al_2O_3-SiO_2 were prepared from metal alkoxide solution using the sol-gel process. After low temperature heat treatments in air, the glasses were heated up to 800° C under a flowing H_2 atmosphere to reduce the Sm^{3+} into Sm^{2+} ions. Samarium ions in the divalent and trivalent states were identified by optical absorption and fluorescence measurements of the glasses. The fluorescence properties of Sm^{2+} ions are discussed in relation to the concentration of Sm_2O_3 and the glass matrix composition. Results of pressure and temperature studies on the luminescence spectra and lifetime of the Sm^{2+} in the glasses are presented as well.

3:30 PM *G2.6
PHOTOCONDUCTIVE STUDIES ON DOPED INSULATORS. Uwe Happek, Department of Physics and Astronomy, The University of Georgia, Athens, GA.

The optical properties of insulators activated with rare earth or transition metal ions are determined by the energy levels of the impurity, and the study of intra-ion transitions has been the principal focus of fundamental research in the past. It has been customary, at least in the physics community, to consider the impurity electrons decoupled from the surroundings, where the host environment influences the impurity electrons via the crystal field, leading to a shift and splitting of the free ion levels [1]. However, it has become evident in recent years that a thorough understanding of the host-impurity system requires the incorporation of excitation processes that involve both the impurity electronic states and the extended states of the host lattice, i.e. the valence and conduction band. This approach leads to a donor-acceptor model for the impurity-host system, similar to the common approach in semiconductor physics [2, 3].
The experimental technique of choice to study delocalized transitions in doped insulators is photoconductivity, a method that allows to determine the position of impurity energy levels with respect to the host bands even for low impurity concentrations (less than 0.1 mol%). Conventionally, this technique is used in semiconductor physics, but a similar, although refined, approach can be applied to insulators as well.
We will discuss examples where the location of impurity energy levels within the band gap of insulators, obtained via photoconductivity, play an important role. These examples include luminescence efficiency of phosphor materials and scintillators, chemical spectral holeburning, excited state absorption in solid state laser, and photovoltaic and photorefractive materials.
[1] B. Henderson and G.F. Imbusch, Optical Spectroscopy of Inorganic Solids, Clarendon Press, Oxford (1989).
[2] W.C. Wong, D.S. McClure, S.A. Basun, M.R. Kotka, Phys. Rev. B51 (1995) 5682.
[3] M. Raukas, S.A. Basun, W. van Schaik, W.M. Yen, U. Happek, Appl. Phys. Lett. 69 (1996) 3300.

4:00 PM G2.7
A NEAR-FIELD OPTICAL INVESTIGATION OF THE LUMINESCENT PROPERTIES OF INDIUM GALLIUM PHOSPHIDE MATERIALS. Charles A. Paulson, Arthur B. Ellis, The University of Wisconsin, Dept of Chemistry, Madison, WI; Thomas F. Kuech, Dept of Chemical Engineering, Madison, WI.

We have used Near-field Scanning Optical Microscopy (NSOM) to study a series of indium gallium phosphide ($In_xGa_{(1-x)}P$) samples grown by liquid phase epitaxy. The concentration of indium in these samples ranged from 33% to 77%. The surface topography is cross-hatched in these samples due to lattice mismatch with the gallium arsenide (GaAs) substrate. The least cross-hatching occurs for samples that contained ~50% indium, where the alloy is nearly lattice matched to the GaAs substrate. Photoluminescence (PL) images gathered using NSOM exhibit strong variations in the optical properties of these samples that are seen to occur in registry with the surface topography, which is simultaneously detected in the NSOM experiment. The PL images show features that are only 100nm across, providing a limit for the optical resolution seen in these experiments. Only weak variations in the PL intensity were seen for the 50% indium sample, while 5-fold changes in the PL intensity are seen on the samples with higher indium concentration. Further, significant shifts in the PL maximum (10 nm shifts) have been observed across the samples with high indium content, once again correlated to the cross-hatch, and probably indicating fluctuations in the percent indium composition, which would correspond to fluctuations in the indium composition of about 1%. Further analyses are performed by

optical microscopy, scanning electron microscopy, atomic force microscopy, and X-ray diffraction, and are collectively used to explain the strong spatial variations in the PL across these samples.

4:15 PM G2.8
ABNORMAL SPECTRAL BEHAVIOR OF TRIVALENT NEODYMIUM IONS IN POTASSIUM YTTRIUM FLUORIDE CRYSTALS. Chunlai Yang, Baldassare Di Bartolo, Department of Physics, Boston College, Chestnut Hill, MA.

KYF_4 is a new kind of fluoride laser crystal. Nd^{3+} ions in KYF_4 crystals have a short lasing wavelength (1040nm), which may be interesting for some special applications. The luminescence lifetime of Nd^{3+} ions in KYF_4 is longer than that of Nd^{3+} in many other laser materials, which make Nd^{3+} doped KYF_4 crystal a good potential material for Q-switched laser operation. In this work we conducted spectroscopic measurements on three Nd^{3+} doped KYF_4 crystals with different concentrations of Nd^{3+} ions (2%, 3%, and 4%), especially, we performed a detailed study on their emission behavior and lifetime behavior at different temperatures in the range 20K to 300K. In this study we found that the Nd^{3+} ions in KYF_4 have an anomalous strong dependence of lifetime and emission intensity on temperature in the range below 100K, which we call as abnormal spectral behavior. Based on the special crystal structure of KYF_4, we proposed an explanation for this abnormal behavior by using an energy transfer model. Nd^{3+} ions in KYF_4 may occupy six different sites, which may be classified into two main sites with significant different environments. Energy transfer is found to take place between the Nd^{3+} ions at these different sites. We derived the formula to describe the deexcitation process and make a data fitting on our dynamic decay measurements. The fitting results indicate that the explaination for the abnormal behavior is reasonable and consistent on both emission spectra and lifetime measurement.

4:30 PM G2.9
INFLUENCE OF PRESSURE ON 5d→4f EMISSION TRANSITIONS. G.B. Cunningham, Y.R. Shen, R.J. Smith, and K.L. Bray, Washington State University, Dept. of Chemistry, Pullman, WA.

The strong parity allowed 5d→4f emission bands of Ce^{3+}, Sm^{2+} and Eu^{2+} have motivated interest in materials doped with these ions as potential phosphors in the visible and ultraviolet. Progress in designing new phosphor materials based on these ions depends on resolving two outstanding fundamental questions concerning the behavior of 5d→4f emission transitions. First, it has been noted experimentally that the efficiency of 5d→4f emission varies widely with host lattice for a given ion. Second, the relationship between 5d→4f emission properties and local coordination geometry, bonding covalency and crystal field strength has not been established. We have recently initiated a new approach, based on high pressure, for understanding the emission properties of luminescent ions. With high pressure, we can systematically vary local coordination geometry, covalency, crystal field strength of luminescent ions as well as electronic states of the host lattice in an attempt to gain new insight into 5d→4f emission transitions. We present recent results of high pressure studies of the 5d→4f emission of Ce^{3+} in Lu_2SiO_5, $Gd_3Sc_2Al_3O_{12}$, Lu_2S_3, and Yb_2SiO_5 and emphasize quenching phenomena. No pressure induced quenching was observed in Ce^{3+}: Lu_2SiO_5 and Ce^{3+}: $Gd_3Sc_2Al_3O_{12}$, while significant quenching was observed in Ce^{3+}: Lu_2S_3. We attribute the quenching of Ce^{3+}: Lu_2S_3 to photoionization resulting from a pressure induced electronic crossover of the conduction band edge of the host lattice and the 5d emitting state of Ce^{3+}. In contrast to isostructural Lu_2SiO_5, the emission of Ce^{3+} in Yb_2SiO_5 is weak at ambient conditions and remains weak upon increasing pressure. Based on the high pressure results, we attribute the weak intensity of Ce^{3+}:Yb_2SiO_5 to an electron transfer from Ce^{3+} to Yb^{3+}. We also discuss a pressure-induced electronic crossover of the $4f^5$5d and lowest excited $4f^6$ ($^5D_0$) state of Sm^{2+} in SrFCl and stabilization of $4f^5$5d→$4f^6$($^7F_0$) emission.

SESSION G3: POSTER SESSION
Chairs: Lori R. Brock and A. Srivastava
Tuesday Evening, April 17, 2001
8:00 PM
Metropolitan Ballroom (Argent)

G3.1
ENHANCEMENT OF LUMINESCENCE FOR ORGANIC AND INORGANIC SURFACE PASSIVATED ZnS QUANTUM DOTS. Hatim Mohamed El-Khair, Ling Xu, Minghai Li, Xinfan Huang, and Kunji Chen, State Key Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing, P.R. CHINA.

Recent studies on type II-VI semiconductors QDs, such as CdS and CdSe, have shown interested optical properties afforded by their tunable size due to the confinement of electronic wave functions. However, surface states such as dangling bonds and recombination trap states of different energies can reduce luminescence efficiency and hence limited their applications of QDs. Various studies have shown that appropriate surface passivation can substantially suppresses surface trapping and result in the enhancement of luminescence. In this report ZnS semiconductor quantum dots (QDs) have been synthesized by colloidal chemical method using inorganic reagents. Then polystyrene (PS) and silica were used as organic and inorganic surface passivation agents to prepare ZnS/PS and ZnS/SiO_2 QDs respectively. TEM results show that the QDs sizes is monodispersed ranging from 1 to 3 nm. Due to quantum confinement effects, small changes in QDs size allow for dramatic changses in optical properties. The absorbance and emission maxima at about 320 and 340 nm for ZnS/PS and ZnS/SiO_2 QDs are blue shifted from its bulk materials confirming the quantum size effect. Band edge emissions intensities enhanced as much as 8-10 times for ZnS/SiO_2 and 10-15 times for ZnS/PS QDs. This could be interpreted that: coating ZnS core with a wider bandgap material SiO_2 or organic polystyrene substantially suppresses surface radiative and nonradiative centers and result in the enhancement of band edge emission of ZnS QDs.

G3.2
LUMINESCENCE OF SILICON AND SILICON ON INSULATOR LAYERS IMPLANTED WITH HYDROGEN IONS. V.P. Popov, I.E. Tyschenko, K.S. Zhuravlev, L.N. Safronov, Institute of Semiconductor Physics, Novosibirsk, RUSSIA; I.I. Morosov, Institute of Nuclear Physics, Novosibirsk, RUSSIA; A. Misiuk, Institute of Electron Technology, Warsaw, POLAND.

Photoluminescence (PL) properties of Si:H layers on Si and SOI wafers implanted with hydrogen ions at an energy of 24 keV to doses of (0.6 - 3.0) x 10^{17} cm^{-2} were studied. The H implantation was carried out with ion-plasma source. Subsequently, the samples were annealed at the temperatures, ranging from 200 to 1000°C during 1 hour in N_2 or Ar ambient, at pressures of 1 bar and 11.4 kbar. Emission PL spectra were excited with N_2 -laser wavelength of 337 nm at room temperature. The as-implanted samples exhibited the broad weak-intensity PL band in the wavelength range between 400 and 800 nm. The PL intensity increased with raising annealing temperature. Maximum of PL intensity was obtained from the samples annealed at the temperature of 600°C. As the hydrostatic pressure was raised to 11.4 kbar the PL peaks of around 420 and 570 nm were dominant in PL spectra after annealing 600°C for SOI and Si wafers respectively. Unusual phenomenon of enhanced interference at the interval 450 - 750 nm appeared in the SOI wafers after high pressure treatment. The nature of the photoluminescence is discussed.

G3.3
RECOMBINATION LUMINESCENCE IN $LiBaF_3$ CRYSTALS. Peter Kulis, Uldis Rogulis, Maris Springis, Ivars Tale, Aris Veispals, Institute of Solid State Physics, University of Latvia, Riga, LATVIA.

$LiBaF_3$ represents a group of materials, prospective as scintillators and as radiation memory materials for dosemetric and imaging purpose. Well-known fast cross luminescence (CL) bands in ultraviolet [1] and the broad self-trapped exciton luminescence (STE) [2] as well as Ce^{3+} emission in $LiBaF_3$ are promising features for thermal -neutron and gamma-rays detection. Owing the sensitivity of $LiBaF_3$ to impurities it was possible to increase the Ce^{3+} emission and to shorten STE decay component by co-doping of $LiBaF_3$:Ce with K^+ and Rb^+ [3]. Radiation energy is stored mainly by creating of the F-type centers [4]. Recombination luminescence is one of the most sensitive phenomena promising for read-out. In the present paper we report on the investigation of the radiative recombination processes in oxygen contaminated $LiBaF_3$ crystal by means of the EPR, luminescence afterglow, thermostimulated luminescence (TSL) and photoluminescence (PL). X- irradiation below 170 K results in creation of a temperature -independent afterglow (TL) due to the tunneling recombination between close electron and hole centers. The F-type centers and the V_K centers are the tunneling recombination partners, responsible for the 4.1 eV band which dominates in TL spectrum at temperature below 130 K as well as in the TSL peak at 125 K. The luminescence band at 3.15 eV caused by charge-transfer transition between F-type and oxygen centres dominates in both TL and TSL spectra at temperatures above 130 K. 1. P.A. Rodnyi, M.A. Terekhin and E.N. Melchakov, J. Lumin. Vol. 47, 281 (1991). 2. I. Tale, P. Kulis, et al. J. Lumin. Vol. 72-74, 722 (1997). 3. C.M. Combes, Phd. thesis, p.115 (1999). 4. P. Kulis, I. Tale, et al. Radiation Effects & Defects Sol. Vol. 149, 97 (1999).

G3.4
PL DUE TO DISCRETE GAP LEVELS IN SOME CHALCOGENIDE GLASSES - A CONFIGURATIONAL COORDINATE DIAGRAM ILLUSTRATION. N. Asha Bhat, K.S. Sangunni and K.S.R.K. Rao, Dept of Physics, Indian Institute of Science, Bangalore, INDIA.

Amorphous chalcogenide semiconductors show characteristic broad photoluminescence (PL) with a large Stoke's shift of half the band gap magnitude. Presence of various inherent charged defects such as D^+ and D^-, also known as valence-alternation pairs, have been contemplated to be the origin of PL in these semiconductors. However, featureless broad spectra observed in the past for almost all these semiconductors has impeded the distinction between various inherent defects as radiative recombination centers. Recently, we have observed some fine structure with three separate transitions in the broad PL spectrum (0.7eV to 1.2eV) of some of these semiconductors namely a-Se, $Ge_{20}Se_{80}$ and $Ge_{20}Se_{70}Te_{10}$ and a few Bi doped $Ge_{20}Se_{80}$ and $Ge_{20}Se_{70}Te_{10}$. The fine structure observed is very interesting as it provides the first-ever direct evidence for the presence of discrete gap levels. The features associated with the fine structure such as peak energy position and width are extracted by deconvoluting the experimental spectra reveal that one of the three transitions is insensitive to the addition of dopants. Based on this fact, the particular transition is attribute to the recombination of electrons and holes trapped at intimate valence-alternation pairs, which are nothing but paired D^+ and D^- defects. Out of the remaining two transitions, one can be due to the recombination of electron trapped at shallow electron trap with a free hole and the other can be due to the recombination between free electrons and holes trapped in shallow levels. In the latter two transitions the unpaired D^+ and D^- defects can act as shallow traps for electrons and holes, respectively. The multiple transitions discussed above are illustrated, for the first time, with a configurational coordinate diagram representation to have a better understanding about the gap levels as recombination centers in chalcogenide glasses.

G3.5

LUMINESCENCE AS A PROBE IN CRYSTALLINE EUROPIUM DOPED TITANIA MATERIALS. James Ovenstone, Philip J. Titler, Robert Withnall and Jack Silver, University of Greenwich, School of Chemical and Life Sciences, London, UNITED KINGDOM.

Titania has three naturally occurring polymorphs, anatase, brookite and rutile, however, distinguishing between the former two can be difficult, since all the major XRD and Raman lines overlap with each other. We have used a Raman spectrometer to investigate the luminescence of the different crystalline phases of titania doped with europium. By studying the up conversion spectra of europium doped titania, we can easily track the crystallisation process of anatase and brookite, and the subsequent phase changes to form pure anatase and then rutile during calcination. Despite the poor down conversion brightness of doped crystalline titania materials, their luminescence can be used as a useful tool to study the behaviour of dopants in the lattice. From the down conversion spectra, we have shown that the brookite lattice contains two accessible sites for cation dopants, while the anatase and rutile polymorphs each contain only one (confirmed by Mossbauer spectroscopy). Furthermore, in addition to the symmetry information gained about the titania lattice from the Raman bands of each phase, the luminescence bands of the up conversion spectra can give us useful information about the symmetry of the cation holes (in which the europium ions are situated) in the lattice. We have shown from the increasing number of emission lines, that the symmetry of the holes increases markedly with increasing calcination temperature, and the transformation from brookite to anatase and then to rutile. These results show the potential wealth of information which can be obtained from the addition of a small amount of dopant into a lattice to cause luminescence.

G3.6

ENHANCEMENT OF CATHODOLUMINESCENCE CHARACTERISTIC FROM $CaTiO_3:Pr^3$, BY Ga^3 ADDITION. Jung-Woo Byun, Dong-Kuk Kim, Byung-Kyo Lee, Dept of Inorganic Materials Engr., Kyungpook Natl. Univ., KOREA; Seong-Gu Kang, Dept of Chemical Eng., Hoseo Univ., KOREA; Seung-Youl Kang, Kyung-Soo Suh, ETRI, KOREA.

$CaTiO_3:Pr^{3+}$ as an oxide compound phosphor is expected to be applied for a field emission display (FED) due to its relatively high conductivity. For the practical use, however, the CL intensity of $CaTiO_3:Pr^{3+}$ has to be enhanced. We introduced Ga^{3+} as a co-activator into the phosphor and investigated the CL characteristics with various Ga^{3+} concentrations. The phosphor was obtained by solid-solid reactions at 1200°C for 4hrs and the activator and the co-activator concentrations were optimized at maximal intensity of cathodoluminescence and photoluminescence. The $CaTiO_3:Pr^{3+}$ phosphor was characterized by a red emission at 614nm corresponding to the $^1D_3 \rightarrow {}^3H_3$ inner transition of Pr^{3+}. The CL intensity of $CaTiO_3:Pr^{3+}$ was remarkably increased when Ti^{4+} atom was replaced by the Ga^{3+}. When the Ga^{3+} concentration is 5 times of Pr^{3+} molar concentration, the emission intensity of the $CaTiO_3:Pr^{3+}$ phosphor with Ga^{3+} is about 5 times higher than Ga^{3+}-free samples. So, it was concluded that the addition of Ga^{3+} is essential to enhance CL property at low voltage. From the analysis of this enhancement of CL properties, the following mechanism is proposed. Excitation into the host lattice leads to the formation of electrons in the conduction band and holes in the valence band. The electrons in the conduction band recombine with the holes trapped at Ga^{3+} and this energy is effectively transferred to Pr^{3+} ion, which gives its own characteristic red emission.

G3.7

MORPHOLOGY AND CATHODOLUMINESCENCE OF Li-DOPED $SrTiO_3:Pr^3,Ga^3$, A RED PHOSPHOR OPERATING AT LOW VOLTAGES. Jin Young Kim, Duk Young Jeon, Dept. of MS&E, KAIST, KOREA; Seong-Gu Kang, Dept. of Chemical Eng., Hoseo Univ., KOREA; Seung-Youl Kang, Kyung-Soo Suh, ETRI, KOREA.

Li doped $SrTiO_3:Pr^{3+},Ga^{3+}$ has been investigated as a red phosphor for the application to VFDs and FEDs. In $SrTiO_3:Pr^{3+},Ga^{3+}$ system, Pr^{3+} can substitute for Sr^{2+} because the ionic radius of Pr^{3+} almost coincides with that of Sr^{2+}. However, it was found that only a small fraction of Pr ions are incorporated in the $SrTiO_3$ lattice by XRF analysis of $SrTiO_3:Pr^{3+},Ga^{3+}$ single crystal. In the present study, the effect of Li addition into $SrTiO_3:Pr^{3+},Ga^{3+}$ on the cathodoluminescence(CL) properties was examined at low acceleration voltage. Especially, thanks to the liquid phase of Li_2CO_3 during the sintering process, doped Li^+ ions act as a lubricant for the efficient incorporation of Pr ions into $SrTiO_3:Pr^{3+},Ga^{3+}$ lattice. And also, the dissolution of sharp edges of particulate solids makes the particle surfaces smoother, followed by the formation of larger grains with a rounded shape through the flux effect of Li. In conclusion, the previous two effects by Li addition could strongly enhance the low-voltage CL efficiency of $SrTiO_3:Pr^{3+},Ga^{3+}$ phosphors.

G3.8

LUMINESCENT PROPERTIES OF AMORPHOUS AlN AND ALLOY THIN-FILM PHOSPHORS DOPED WITH RARE-EARTH AND TRANSITION METALS. M.L. Caldwell, M.E. Kordesch, P.G. Van Patten, H.H. Richardson, Ohio Univ, Condensed Materials and Surface Science Program, Athens, OH.

Thin films ($\sim$ 200 nm) of amorphous AlN and $Al_xGa_{1-x}N$ doped with Er, Tb, Cu, Mn and Cr have been grown by RF magnetron reactive sputtering at 77 and 300 K. The doped amorphous AlN films were "activated" at temperatures up to 1250 K in a nitrogen atmosphere and showed luminescence in the visible spectrum when excited with 2.85 kV electrons. Colors ranging from blue to red (420 nm - 690 nm) have been observed from the luminescence of Tb, Er, Cu, Mn, and Cr. Electroluminescent devices have been fabricated using a glass substrate with an indium tin oxide transparent bottom electrode and an aluminum top electrode. These devices were inefficient and the phosphor showed poor luminescence efficiencies ($\sim$ 0.03 lm/W). Amorphous $Al_xGa_{1-x}N$ doped with rare-earth and transition metals are promising phosphor materials because the bandgap of the host material can be tuned. Tuning the bandgap alters the luminescence efficiency of the phosphor and could lead to more efficient devices. Because the films can be deposited at 300 K (not at high temperature) and still retain the host properties, the activation process of the luminescent ions is of great technological importance. Infrared microscopy, secondary-ion mass spectrometry, time-resolved photoluminescence spectroscopy and x-ray diffraction have been used to characterize the phosphor activation process. Luminescent properties of amorphous AlN and alloy thin-film phosphors doped with rare-earth and transition metals will be discussed and the activation process will be examined.

G3.9

YTTRIA AND ERBIUM-DOPED YTTRIA THIN FILMS AS OPTICAL WAVEGUIDES. W.H. Kim, C.C. Kim, J.H. Je, Y.S. Kim, Pohang University of Science and Technology, Dept of MS&E, Pohang, SOUTH KOREA.

Er-doped yttria thin films are considered to be attractive photonic materials. We investigated the correlation of microstructure and optical properties for crystalline undoped and Er-doped yttria thin films grown by reactive sputtering. By controlling the processing parameters, a very low optical loss of $\sim$1 dB/cm at 633 nm wavelength could be obtained for undoped films, as grown above 450°C and post-annealed at higher than 500°C. The most important source of the loss was attributed to grain boundary scattering. For Er-doped (0.35 at%) films, the photoluminescence (PL) at 1.54 μm wavelength, which showed a strong intensity at room temperature, significantly enhanced by post-annealing at 600°C in oxygen atmosphere. The fluorescence life time measured at 0.98 μm wavelength also reduced to 0.45 ms while the life time at 1.54 μm wavelength increased to 4.7 ms. We speculate that post-annealing leads to incorporation of Er on well-defined lattice sites, improving the optical properties. The dependence of the dynamical process on the Er content is discussed as well.

G3.10
DIVALENT AND TRIVALENT EUROPIUM DOPED ALUMINA WAVEGUIDES ELABORATED BY PULSED LASER DEPOSITION. Anne Minardi, Claudine Garapon, Jacques Mugnier, CNRS-Lyon1 Univ, Lyon, FRANCE; Corinne Champeaux, CNRS-Univ, Limoges, FRANCE.

Europium doped alumina optical waveguides were prepared by pulsed laser deposition (PLD) using a KrF laser. The targets were obtained by sintering powders synthesized by a sol-gel method. Structural evolution with the oxygen pressure used in the chamber during deposition and the substrate temperature are determined by X rays diffraction and transmission electron microscopy and is shown to go from amorphous to gamma alumina. According to RBS measurements, the films have the same composition as the targets and the doping ions are homogeneously distributed through the film thickness. However, depending to the used oxygen pressure, Eu^{3+} of the doped alumina target may be reduced to Eu^{2+} or keep its three valence in the films. For low pressure (from 10^{-6} to 10^{-4} mbar) only Eu^{2+} is observed, then up to 10^{-2} both valences are present and for pressure above 10^{-1} mbar Eu^{3+} is obtained alone. For Eu^{2+} the 4f-5d broad excitation and emission bands were recorded, peaking at 325 nm and 560 nm respectively. For Eu^{3+} doped films, waveguided fluorescence spectroscopy was used. The usual $^5D_0$ to the ^7F_J multiplets emission spectra were observed. The emission lines are strongly inhomogeneously broadened. Thus low temperature FLN studies were achieved in order to analyze how the different kinds of Eu^{3+} sites may be correlated with the structural evolution induced by the substrate temperature variation. Two families of sites are present. Furthermore, a comparison was done with sol-gel Eu^{3+} doped alumina powders of the same structure.

G3.11
THEORETICAL MODEL OF LUMINESCENCE AND PHOTO-CONDYCTIVITY OF POLY-N-EPOXYPROPYLCARBAZOLE WITH INTRAMOLECULAR CHARGE TRANSFER COMPOUNDS. Oleksandr Olishevskyy, Kyiv Univ, Dept of Physics, Kyiv, UKRAINE.

Features of charges photogeneration in the amorphous molecular semiconductor films based on polyepoxypropylcarbazole containing compounds with intramolecular charge transfer used in holographic recording media are investigated in theory. It was shown that the efficiency of charge carriers photogeneration is proportional to a difference between the ionization potential of the molecules of compounds with intramolecular charge transfer and polyepoxypropylcarbazole nuclei. Influence of an external electric field on the quantum yield of charges photogeneration and photoluminescence as studied. In an external electric field the potential barrier transparency increases for tunneling transition of holes and electrons to the neighbor donor and acceptor molecules. When the charge carries mobilities is small the life time of carriers is greater than the time of spin-lattice relaxation. So this is the cause both of paramagnetic particles accumulation in the volume of the amorphous molecular semiconductor film.

G3.12
ELECTRICAL AND OPTICAL STUDIES OF THE ORGANIC THIN FILM DEVICES PRODUCED BY CLUSTER BEAM DEPOSITION METHODS. Jae-Yoo Kim, Moonhee Kim, Jong-Ho Choi, Korea University, Dept of Chemistry, Seoul, KOREA; Jae-Kwang Lee, Hun-Mo Kim, Jinsoo Joo, Korea University, Dept of Physics, Seoul, KOREA.

Organic thin films of anthracene, tetracene, pentacene and Alq_3 have been fabricated by applying novel neutral and ionized cluster beam deposition (NCBD and ICBD) methods. The surface morphology measurements show that the cluster beam is extremely efficient in preparing well-defined flat and smooth surfaces. The investigations of the electric and optical characteristics such as I-V characteristic, AC impedance in the range of 10 Hz $\sim$ 2 MHz, photo- and electro-luminescence (PL and EL) will be presented. In addition, the organic light emitting devices (OLEDs) with the structure of ITO/poly[2-(N-carbazolyl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]/organic layer/Li:Al have been fabricated by applying cluster beam methods and their device properties such as EL, PL, external quantum efficiencies(EQE), I-V characteristic etc. were examined. We also introduced the DCM dopant into organic layer and found lower turn-on voltage, higher EQE and color tuning capability.

G3.13
POLYGERMYNE: GERMANIUM SHEET POLYMERS WITH EFFICIENT NEAR-INFRARED LUMINESCENCE. Günther Vogg, Martin S. Brandt, Martin Stutzmann, Walter Schottky Institut, Garching, GERMANY.

Silicon sheet polymers such as siloxene have been known to exhibit strong visible photoluminescence. It was further shown that the energy of the photoluminescence could be tuned by ligand substitution. Synthesizing germanium and silicon-germanium sheet polymers for the first time, we show here that the PL energy can similarly be influenced by substitution in the backbone of the polymer. Polygermyne $(GeH)_2$ films were prepared in a two-step process: $CaGe_2$-films were first grown on crystalline Ge substrates via reactive deposition epitaxy followed by a topochemical transformation in HCl at low temperatures. Using (111)-oriented Ge substrates, epitaxial crystalline polygermyne films with the Ge layers parallel to the substrate surface are formed as shown by X-ray diffraction. Polygermyne exhibits a strong photoluminescence at 1.3 to 1.4 eV and a direct bandgap at 1.6 eV. In contrast to the corresponding silicon sheet polymers, virtually no oxygen is incorporated into polygermyne during the topochemical transformation, leading to an increased stability of the material. Using $Si_{1-x}Ge_x$ alloys as the starting substrates, the corresponding $Ca(Si_{1-x}Ge_x)_2$ Zintl phases as well as polygermanosilynes can be prepared. Adjusting the alloy composition, the photoluminescence of these sheet polymers can be tuned between 2.4 and 1.3 eV.

G3.14
PHOTOPHYSICAL PROPERTIES AND ELECTRO-LUMINESCENCE OF LANTHANIDE ORGANOMETALLIC COMPLEXES. Francesco Meinardi, Antonio Papagni, Marco Salina, Sylke Blumstengel, Adele Sassella, Alessandro Borghesi and Riccardo Tubino, Dipartimento di Scienza dei Materiali, Universita di Milano-Bicocca, Milano, ITALY; Guglielmo Lanzani, Dipertimento di Fisica, Politecnico di Milano, ITALY.

In the field of OLED's, stable rare earth ions complexes bearing conjugated ligands are receiving increasing attention since they combine the advantages of the organic ligands (high absorption cross section, solubility, etc.) with those of the inorganic component (sharp emission bands, long lifetimes). In these systems the excited state levels of the emitting ion are populated by an efficient intramolecular energy transfer - probably involving triplet states - from the optically (or electrically) excited ligand. As both the absorption of the organic ligand and the emission of the lanthanide ion can be tuned, a variety of materials exhibiting a wide range of optical properties can be envisaged. As an example, Er 3 complexes give access to the emission in the IR region not reached by all-organic dyes. The photophysical properties of Eu 3 and Er 3 complexes containing quinoline and phenanthroline based ligands have been investigated with both cw and time-resolved photoluminescence, as well as with pump and probe techniques with femtosecond resolution. The position and the lifetimes of the intermediate excited states involved in the energy transfer is measured and their role in determining the quantum yield of the photo- and the electro-luminescence in these materials is discussed.

G3.15
NOVEL BLUE EMITTING DEVICE FOR FULL COLOR OLED. Sung Han Kim, Han Sung Yu, Yun Soo Choe, Samsung SDI Coporation, OLED Team, Suwon, KOREA; Soon Ki Kwon, Yun Hi Kim, Dong Cheol Shin, Hyun Woon Lee, Gyeongsang National University, Dept of Polymer Engineering, Chinju, KOREA.

The new blue light-emitting device for full color display was successfully developed. With newly designed blue material, spirobifluorene derivative, and multi-layer device stucture, it was possible to get a luminance efficiency of 1.22 lm/W at a voltage and brightness of 7.7V and 300cd/m2, The most important result was the achievement of pure blue emission (0.14, 0.08) nearest to the NTSC standard among ever reported.

SESSION G4: NANOCRYSTALLINE MATERIALS
Chair: Peter C. Schmidt
Wednesday Morning, April 18, 2001
Franciscan II (Argent)

8:30 AM *G4.1
LIQUID-PHASE SYNTHESIS AND LUMINESCENCE OF COLLOIDAL LANTHANIDE-DOPED NANOCRYSTALS. K. Riwotzki, H. Meyssamy, A. Kornowski, M. Haase, Institut für Physikalische Chemie, Universität Hamburg, Hamburg, GERMANY.

Colloidal solutions and redispersible powders of nanocrystalline, lanthanide-doped phosphates have been prepared in high-boiling coordinating solvents. Highly crystalline materials in the high-temperature phases were obtained at temperatures as low as 200°C. The synthesis yields gram amounts of well-separated nanoparticles with a very narrow size distribution and a mean diameter of 5 nm. By analyzing the line splitting and the intensity pattern in the luminescence spectra of europium-doped samples, we are able to verify that the dopant ions enter the same lattice sites as in the corresponding bulk material.

The materials are compared with hydrothermally prepared nanoparticles and nanofibers of lanthanide-doped YVO_4 and $LaPO_4$. Transfer of excitation energy to the dopant ions is observed in all systems investigated. $LaPO_4$: Ce, Tb nanoparticles show energy transfer between cerium and terbium and exhibit a quantum yield of up to 62%. The quantum yield strongly depends on surface properties of the particles.

9:00 AM G4.2
SURFACE MODIFICATION OF CADMIUM SELENIDE NANOCRYSTALS BY ORGANIC LIGANDS. Chunxin Zhang, Lajos Balogh, University of Michigan, Center for Biologic Nanotechnology, Scott E. Woehler, College of Pharmacy, University of Michigan, Ann Arbor, MI; Stephen O'Brien, Columbia University, Department of Applied Physics; Louis E. Brus, Columbia University, Department of Chemistry, New York, NY.

Surface modification of nanoparticles with organic ligands is an important issue in quantum dot chemistry, because the surface bound organic groups determine both the stability of the nanoparticles and their compatibility with the actual environment as well as influence their quantum efficiency. In this work trioctylphosphine oxide (TOPO) capped CdSe crystalline nanoparticles (4-15 nm) were used as a model system to investigate the exchange of surface groups. Both physical and chemical binding were explored by using several ligand functions including -COOH, -SH, pyridine and primary amine. Ligand carriers involved small organic molecules as well as dendritic polymers. The nanoparticles were characterized by AFM and spectroscopy methods. Cap exchange was monitored by 1H, 13C, 31P and 14N NMR, as well as by other spectroscopic methods. Crucial parameters of preparation, such as purity of chemicals, and major methods of cap exchange using small molecular and macromolecular ligands will be discussed.

9:15 AM G4.3
STRONG BLUE PHOTO- AND ELECTROLUMINESCENCE FROM TIN IMPLANTED SILICON DIOXIDE. L. Rebohle, T. Gebel, J. von Borany, M. Klimenkov, W. Skorupa, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, GERMANY; H. Fröb, Institute of Applied Photo Physics, TU Dresden, Dresden, GERMANY.

We have obtained strong blue photo- and electroluminescence at room temperature from tin nanostructures using a dry technology compatible to microelectronic manufacturing. Thermally grown, 100 and 200 nm thick SiO_2-films are implanted with $10^{15}...10^{16}$ cm^{-2} Sn^+-ions in the energy range of 60 to 130 keV, followed by different annealing procedures. Photoluminescence (PL), Electroluminescence (EL), Current-Voltage and Capacity-Voltage measurements, High-Resolution Transmission Electron Microscopy and Rutherford Backscattering Spectrometry are used for sample characterization. Whereas the PL spectrum was recorded under 250 nm excitation, the EL spectrum was obtained using an ITO front contact and an electric field of about 6 to 8 $MVcm^{-1}$. Both spectra are compared and their dependence on preparation and excitation conditions are discussed. First results give power efficiencies up to $5 \bullet 10^{-4}$ for the EL. It will be shown, that the luminescence is caused by triplet-to-singlet transition of an oxygen deficiency center, where at least one Si atom is replaced by a Sn atom. To understand the charge carrier transport and the electrical excitation mechanism of the luminescence centers, Current-Voltage and Capacity-Voltage measurements were carried out and their results were correlated with the EL features. Two possible excitation mechanism, namely impact excitation by hot electrons and field ionization of the luminescence centers, are discussed.

9:30 AM G4.4
LUMINESCENCE OF Lu_2O_3:Tm^{3+} NANOPARTICLES. Celso de Mello Donegá, Andries Meijerink, Debye Institute, Dept of Condensed Matter, Utrecht University, Utrecht, THE NETHERLANDS; Eugeniusz Zych, Faculty of Chemistry, Wroclaw University, Wroclaw, POLAND.

Nanostructured materials have attracted great interest in recent years because their properties are markedly different from those of bulk materials. These differences arise from several effects: larger surface to volume ratio, quantum confinement and geometrical confinement of phonons. The vast majority of the investigations have been focused on metals and semiconductors, rather than on insulators, even though many important commercial phosphors belong to this latter class of materials. In this paper we compare the luminescence of nanoparticles and micrometer sized particles of $(Lu_{1-x}Tm_x)_2O_3$ (x= 0.001- 0.05). The nanoparticles are ~30 nm in diameter and were prepared by a combustion technique using urea as fuel and lanthanide nitrate as oxidizer. To promote further growth of the nanoparticles the samples were subjected to a thermal treatment (1473 K - 4 h, followed by 1273 K - 10 h). The luminescence of all samples upon UV excitation consisted of several lines originating from the $^1D_2$ level of Tm^{3+}. Weak $^1G_4$ lines are also present. A broad emission band (λ_{max}=440 nm; FWHM ~5000 cm^{-1}), whose intensity is independent on the Tm concentration, is also observed. This band is assigned to defect related luminescence. After the thermal treatment the broad band intensity decreases, whereas the Tm^{3+} f-f emission intensity increases. This observation can be ascribed to the decrease of the defect concentration after the treatment. The concentration quenching is less pronounced for Tm^{3+} in the nanoparticles, starting above 1 mol%, whereas in the particles after the treatment it is observable above 0.1 mol%. This shows that the cross-relaxation (CR) processes responsible for the quenching of the Tm^{3+} luminescence are less effective in the nanoparticles, probably because of a lower pair concentration.

10:15 AM G4.5
SYNTHESIS AND LUMINESCENT PROPERTIES OF COLLOIDAL LANTHANIDE DOPED YVO_4. Arnaud Huignard, Thierry Gacoin, Frederic Chaput, Jean-Pierre Boilot, Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, Palaiseau, FRANCE; Patrick Aschehoug, Bruno Viana, Laboratoire de Chimie de l'Etat Solide, ENSCP, Paris, FRANCE.

Luminescent nanoparticles are very promising materials to be incorporated into new optical devices or to be used as biological labels. Up to now, the work on this kind of nanoparticles has been mainly limited to II-VI semiconductors. However, at the bulk state, one of the most efficient class of luminescent materials is the lanthanide doped oxides. This paper is therefore devoted to the synthesis through colloidal chemistry of nanoparticles of lanthanide doped yttrium orthovanadate (YVO_4:Ln), a well known material under its bulk form for its phosphor (Ln = Eu) or laser (Ln = Nd) properties. First, we developed an aqueous synthesis, based on precipitation reactions at room temperature. It leads to highly concentrated (up to 1 $mol.l^{-1}$) and well-dispersed solutions of crystalline nanoparticles of 5 to 30 nm in size. A detailed study of the luminescence properties in the case of YVO_4:Eu colloidal solutions was carried out. In comparaison with the bulk material, a lower quantum yield as well as a higher concentration quenching were observed. These differences were explained by varying some characteristics of the colloidal solutions such as the crystallinity and the surface environment. When these parameters are optimized, the quantum yield was found to be as high as 38% for the $Y_{0.85}Eu_{0.15}VO_4$ composition. Secondly, the YVO_4:Ln (Ln = Eu, Nd) nanoparticles were incorporated into silica sol-gel matrices. In order to ensure the stability of the nanoparticles in the matrices, a grafting of organic species at the surface was found to be necessary. Through this method, transparent sol-gel thin films and monoliths doped with the YVO_4:Ln nanoparticles can be obtained. The optical properties of such materials as well as their potentiality as laser devices will be discussed.

10:30 AM G4.6
LUMINESCENCE OF NANOCRYSTALLINE ZNS:Cu. A.A. Bol, J.A. Bergwerff, A. Meijerink, Utrecht University, Debye Institute, Department of Condensed Matter, Utrecht, THE NETHERLANDS.

During the period from the 1950s to the 1970s much research has been done on the luminescence of bulk ZnS:Cu, which is a well-known CRT phosphor. Besides, the electroluminescence (EL) of bulk ZnS:Cu is widely studied for possible applications in EL devices. Recently, the luminescence of nanocrystalline ZnS:Cu has been investigated. Due to the large surface to volume ratio of these nanoparticles, charge carriers can be better injected into the electroluminescent material. This could make nanocrystalline semiconductors better suited for EL devices than bulk materials. To use these materials in such applications it is important to investigate the effects of the particle size on the luminescence of these materials. Up till now, only a green luminescence was reported for nanocrystalline ZnS:Cu, while for bulk ZnS:Cu also a blue, red and IR emission is observed. In this contribution a red emission is detected for nanocrystalline ZnS:Cu. At 4 K three emissions are observed: a blue (425 nm), a green (470 nm) and a red (590 nm) emission. The blue emission (λ_{exc}=320 nm) is attributed to a defect related emission of the ZnS host. The green and red emission, which are also observed for bulk ZnS:Cu, are assigned to the transition between, respectively, a shallow and deep trap of the semiconductor and the t2 energy level of the copper. Both emissions could be excited most efficiently at 355 nm, but also under excitation of the ZnS host (λ_{exc}=320 nm). The green luminescence quenches at lower temperature than the red emission. At room temperature only the red emission is visible. This is in contrast with earlier publications. The differences in quenching temperatures could be explained by photoionization. The quenching temperature is dependent on the bandgap of the host material and is therefore sensitive to the particle size of the nanocrystalline semiconductor.

10:45 AM G4.7
LUMINESCENCE OF NANOCRYSTALLINE ZnS:Pb^2. A.A. Bol, A. Meijerink, Utrecht University, Debye Institute, Department of Condensed Matter, Utrecht, THE NETHERLANDS.

Efficiently luminescing doped semiconductor nanocrystals are important in applications like electroluminescent devices. In addition to properties which are important for applications, it is interesting to investigate the effects of the particle size and quantum size effects on the luminescence of these materials. Up till now, only the luminescence of nanocrystalline ZnS:Mn^{2+} has been studied extensively. This contribution deals with the luminescence of a different material, namely, nanocrystalline ZnS:Pb^{2+}. Nanocrystalline ZnS:Pb^{2+} exhibits a very broad white emission under 380 nm excitation or a red emission under 480 nm excitation. These emissions were also found for bulk ZnS:Pb^{2+}. The intensity of the red emission is influenced by the synthesis procedure (e.g. Zn/S ratio) and by heat treatments of the samples. The red emission possibly originates from a Pb^{2+} ion located on a regular Zn^{2+} site and resembles properties typically for A-band transitions of Pb^{2+} ions. The white emission consists of two emission bands: a green and a red band. The green emission probably originates from a charge-transfer like D-band emission. The exact origin of this emission is unknown. The green emission overlaps with the excitation spectrum of the red emission and therefore the red emission is also visible upon excitation at 380 nm. At 4 K the quantum efficiency of the white emission is close to 100%. The quantum efficiency at room temperature is about 5%, which is high in comparison to a comparable system of nanocrystalline ZnS:Mn^{2+}. With increasing temperature both emissions quench, possibly due to photoionization. The quenching temperature is dependent on the band gap of the host material and is therefore sensitive to band gap widening due to quantum size effects. For a smaller particle size of the nanocrystalline semiconductor the quenching temperature increases.

11:00 AM G4.8
SYNTHESIS AND LUMINESCENCE OF DOPED ZnSe NANOCRYSTALS. J.F. Suyver, S.F. Wuister, J.J. Kelly, A. Meijerink, Debye Institute, Physics and Chemistry of Materials, Utrecht University, THE NETHERLANDS.

Fascinating applications have been promised for (doped) semiconductor nanocrystal composites, such as electroluminescent devices, laser materials and biological labeling. Many of these applications require the efficient injection of charge carriers into the nanocrystal valence- and conduction bands, followed by efficient energy transfer to a luminescent ion present in the nanocrystal. One of the most promising II-VI materials therefore is ZnSe, due to its relatively high valence bandedge, which will allow efficient hole injection. Until now, not much research on the luminescence properties of doped ZnSe powders has been performed. Powders of ZnSe nanocrystals with a typical radius of 4 nm doped with Mn^{2+} or Cu^{+} have been fabricated via an inorganic chemical synthesis based on the TOP/TOPO method. Hexadecylamine instead of TOPO was used as the solvent due to its weaker bond with Zn. The synthesis and the nanocrystal properties are discussed. Luminescence excitation spectra show that the dopant is excited via energy transfer from the ZnSe host lattice. For the ZnSe:Mn^{2+} samples, both the Mn^{2+} emission wavelength and the luminescence lifetime is found to depend on the Mn^{2+} concentration incorporated into the nanocrystal and total luminescence quantum efficiencies of 2-3 % have been obtained. The temperature dependence of the ZnSe related emission is described well by models developed for bulk semiconductors. Between 4 K and room temperature, the Mn^{2+} emission energy has a blue-shift of ~15 meV, which is slightly less than that measured for the bulk system. The Cu^{+} photoluminescence is dependent on the particle size and shows a temperature quenching behavior with an activation energy of ~190 meV. Based on these results a luminescence mechanism of the ZnSe:Mn^{2+} and ZnSe:Cu^{+} nanocrystals is presented. Finally, expectations for future applications are briefly discussed.

11:15 AM G4.9
PRESSURE TUNING SPECTROSCOPY OF Mn^{2+} IN BULK AND NANOCRYSTALLINE SULFIDE SEMICONDUCTORS. Randy J. Smith, Yongrong Shen, and Kevin L. Bray, Washington State University, Department of Chemistry, Pullman, WA.

Mn^{2+}:ZnS is widely used as a phosphor in CRTs and EL displays. The success of Mn^{2+}:ZnS has motivated efforts to shift or broaden the $^4T_1 \rightarrow {}^6A_1$ emission of Mn^{2+} to achieve a wider range of colors for phosphor or filtered white light displays. The emission properties of Mn^{2+} can be tuned by chemically modifying the ZnS host lattice or by preparing the nanocrystalline form. Recent work has shown that alloying ZnS with Ga leads to a red shift of the Mn^{2+} emission. Higher excitation efficiencies have been reported for nanocrystalline Mn^{2+}:ZnS.
We present recent high pressure luminescence results on the emission of Mn^{2+} in bulk ZnS, $Zn_{1-3x/2}Ga_xS$ and nanocrystalline ZnS. Our objective is to use pressure to systematically vary the coordination geometry, crystal field strength and electronic states of Mn^{2+} as well as the band structure of the host lattice in an attempt to nderstand the chemical and physical factors responsible for determining the emission properties of Mn^{2+}. In nanocrystalline material, pressure will further be used to vary particle size and to explore size-dependent properties induced by pressure.
Initial studies of bulk Mn^{2+}:ZnS and Mn^{2+}:ZnGaS reveal a strong red shift of the $^4T_1 \rightarrow {}^6A_1$ emission of Mn^{2+} with pressure. Pronounced quenching of the Mn^{2+} emission was observed above ~180 kbar in ZnGaS (x=0.3) and was accompanied by a discontinuity in the shift rate of the emission with pressure. We tentatively attribute the quenching to a pressure-induced phase transition from a semiconductor to a metallic phase.
Studies of nanocrystalline Mn^{2+}:ZnS are underway. Particle sizes of 1, 3, 5, and 10 nm have been prepared. The effect of pressure on the emission intensity, emission energy and bandgap will be discussed and correlated with estimated pressure-induced reductions in particle size. The variation of the phase transition pressure with particle size will also be discussed.

SESSION G5: SYNTHESIS & PROCESSING
Chair: Joanna M. McKittrick
Wednesday Afternoon, April 18, 2001
Franciscan II (Argent)

1:30 PM G5.1
CERIUM DOPED GARNET PHOSPHORS FOR APPLICATION IN WHITE GaN-BASED LEDS. Jennifer L. Wu, Dept of Chemical Engineering, Steven P. Denbaars, Dept of Materials, Vojislav Srdanov, Dept of Chemistry, University of California-Santa Barbara, Santa Barbara, CA; Henry Weinberg, Symyx Technologies, Santa Clara, CA.

Recently, renewed interest has emerged for the development of visible light, down-converting phosphors for application in white light emitting diodes (LEDs). In such devices, a blue GaN LED can act as a primary light source, serving as an efficient pump to excite photoluminescence in a phosphor with subsequent emission occurring at lower energies. The combination of blue light from the LED chip and emission from the phosphor(s) produces white light. It was recently reported that a combinatorial approach to synthesize and screen potential inorganic phosphors for use in white LEDs could aid in identifying improved phosphors for blue to yellow down conversion. Solid state thin-film arrays (libraries) based on the garnet structure $(A_{1-x},B_x)_{3-z}(C_{1-y},D_y)_5O_{12}:Ce^{3+}{}_z$, where A, B = Y, Gd, Lu, La; C, D = Al, Ga, Sc, B; x and y = 0 to 1.0; and z = 0.03, were synthesized, and x-ray diffraction was used to select library samples of the crystalline garnet phase. Libraries of these various garnets were then characterized spectroscopically and their properties compared to traditionally prepared bulk powder phosphors of similar composition. Emission and excitation trends show that as larger cations are substituted for Y (A = Y), emission and excitation are red-shifted and as larger cations are substituted for Al (C = Al), emission and excitation are blue-shifted. If smaller cations are substituted for Y and Al an opposite trend is observed. Lifetimes and emission/excitation trends are also examined with respect to change in lattice constants for these down-conversion phosphors. Studies show that phosphor composition can be optimized with respect to color point and quantum efficiency. By varying the garnet composition, which controls the color of the white LED, and by taking advantage of the ability to tune the wavelength of blue excitation light through changes in the indium composition of InGaN, a more efficient white LED may be realized.

1:45 PM G5.2
STRUCTURAL AND OPTICAL PROPERTIES OF ZnS:Mn FILMS GROWN BY PULSED LASER DEPOSITION. K.M. Yeung, S.G. Lu, C.L. Mak, K.H. Wong, Department of Applied Physics and Materials Research Centre, Hong Kong Polytechnic University, Hung Hom, Hong Kong, CHINA.

High-quality manganese-doped zinc sulfide (ZnS:Mn) thin films have been deposited on various substrates using pulsed laser deposition (PLD). Effects of back-filled Ar pressure and substrate temperature on the structural as well as optical properties of ZnS:Mn films were studied. Structural characterizations of these films were made by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Optical properties of these films were characterized by photoluminescence (PL) and optical transmittance. Our results reveal that ZnS:Mn films were polycrystalline consisted of a mixed phase structure. The ratio of wurtzite structure to zinc blende structure was strongly depended on the change of substrate temperature as well as back-filled Ar pressure. Higher substrate temperature facilitated the formation of wurtzite structure. Through optimizing the Ar pressure, a ZnS:Mn film with preferred wurtzite structure was obtained at a substrate temperature as low as 450°C. Moreover, experiments indicated that the wurtzite structure has a stronger PL intensity than zinc blende structure. An obvious absorption edge was observed and shifted with the ratio of the two structures.

2:00 PM G5.3
RED EMITTING ELECTROLUMINESCENT DEVICES USING Ga_2O_3 PHOSPHOR THIN FILMS PREPARED BY SOL-GEL PROCESS. Tadatsugu Minami, Tetsuya Shirai, Toshihiro Miyata, Kanazawa Institute of Technology, Optoelectronic Device System R&D Center, Ishikawa, JAPAN.

In this paper, we describe newly developed high luminance red emitting thin-film electroluminescent (TFEL) devices using Cr- or Eu-activated Ga_2O_3 phosphor thin films prepared by a sol-gel deposition method. Single-insulating-layer-type TFEL devices were fabricated by depositing a Ga_2O_3 phosphor thin-film emitting layer onto a thick sintered $BaTiO_3$ ceramic sheet insulating layer. The Ga_2O_3:Cr or Ga_2O_3:Eu thin-film emitting layer was prepared by a sol-gel process using gallium acethylacetonate ($Ga(C_5H_7O_2)_3$) as the Ga source with $Cr(C_5H_7O_2)_3$ or EuCl3 as the dopant source; the Cr or Eu dopant content (Cr/(Cr Ga) or Eu/(Eu Ga) atomic ratio) was varied from 0.1 to 4 atomic%. The ceramic sheet substrates were dipped in the solution, dried and then heat-treated at temperatures of 600-1000°C in air. These processes were repeated 20-25 times in order to obtain a thickness of 1-2 μm. All the dip-coated Ga_2O_3 phosphor thin-film emitting layers were annealed in Ar for 1 h at 870-1100°C. The obtained EL characteristics in the resulting TFEL devices were strongly dependent on the heat treatment and annealing temperatures as well as the dopant content: Cr or Eu. The maximum luminance in a TFEL device with a Ga_2O_3:Cr thin-film emitting layer was obtained with a Cr content of 0.3 atomic%. A high red luminance above 600 cd/m^2 was obtained for a Ga_2O_3:Cr TFEL device driven by a sinusoidal wave voltage at 1 kHz. In addition to these results for Ga_2O_3:Cr TFEL devices, Ga_2O_3:Eu TFEL devices fabricated in the same manner also produced a high red luminance.

2:15 PM G5.4
FAST CERAMIC SCINTILLATOR. Vicente Munné, Jeff E. Nause, Cermet Inc., Atlanta, GA.

A very fast single crystal inorganic scintillator based on ZnO is being made at Cermet using a proprietary pressurized melt apparatus. Crystals are produced from a melt with the addition of a suitable dopant. Several crystal growth parameters and thermal activation schedules have been investigated. Characterization of the crystallinity and purity of the samples has been done by x-ray diffraction and GDMS. In addition, several scintillation parameters have also been investigated.

2:30 PM G5.5
NOVEL FLUORESCENT LABELS DEVELOPED BY LAYER-BY-LAYER ASSEMBLY ON COLLOIDS FOR BIODETECTION SYSTEMS. Wenjun Yang, Dieter Trau, Reinhard Renneberg, Nai-Teng Yu, Dept of Chemistry, Hong Kong University of Science & Technology, Kowloon, Hong Kong, P.R. CHINA; Frank Caruso, Max Planck Institute of Colloids & Interfaces, Potsdam, GERMANY.

Fluorescent microspheres are widely used in biological and immunological studies. There has been intense interest to produce fluorescent particles with a high fluorescence output at a desired excitation wavelength, coupled with surface properties to conjugate such particles with immunoreagents, such as protein. Here we present the preparation and characterization of a novel class of biofunctional fluorescent microparticles for application in immunoassays using the layer-by-layer approach. The layer-by-layer (LbL) assembly of polyelectrolytes onto charged flat or spherical surfaces has been studied extensively recently. It is proved to be a facile method for preparation of colloidal particles with enhanced optical, electrochemical and magnetic properties. The driving force for the sequential adsorption of oppositely charged polyelectrolytes is electrostatic attraction. In this study, multilayers of polycation and different types of polyanions were alternatively deposited onto negatively charged polystyrene latex particles (640 nm in diameter). The polycation used was fluorescein isothiocynate (FITC) labeled poly(allylamine hydrochloride) (PAH) (PAH-FITC). Microelectrophoresis experiments revealed alternating negative and positive zeta-potentials with deposition of each successive polyelectrolyte layer, demonstrating the alternate electrostatic adsorption of polyelectrolytes with opposite charges. Transmission electron microscopy (TEM) images showed a change of the particle surface texture after polyelectrolyte multilayer deposition. Fluorescence microscopy image (FMI) analysis provided direct measurement of the fluorescence intensity of single microparticles. The observed systematic increase of the fluorescence intensity of individual microparticles with increasing PAH-FITC layer number from FMI analysis further demonstrated the controlled regular adsorption of polyelectrolyte layer. The effect of use of different polyanions as the counter part of PAH-FITC was compared. The assembly of immunoglobulin G onto the prepared fluorescent PS microparticles and their potential use was ultimately confirmed by a solid phase immunotest. Construction of such novel and biofunctional fluorescent microparticles promises to have important applications in the field of immunoassays.

2:45 PM G5.6
DEFECTS, PROCESSING AND OPTICAL PROPERTIES OF GaN POWDERS. Jing Tong, Amith K. Murali, Subhash H. Risbud, Univ of California at Davis, Dept. of Chemical Engineering and Materials Science, CA.

Gallium nitride (GaN, as-received) powders were heat-treated under ammonia in a tube furnace to improve optical properties. The heat-treating temperature ranged from 400 to 900°C, and the ammonia flow rate was around 100 ml/min. Chemical analysis showed the nitrogen content of the final products increased from 15.3 to 16.4 weight percent, which implies that the nitrogen vacancies inside GaN had been partially removed. From photoluminescence (PL) spectra, it can be seen that there is a significant change in the optical properties before and after the heat-treatment. The yellow band emission intensity decreased by a factor of about 5 and the near-band-edge emission intensity increased by a factor of about 4. This seems to indicate some deep level impurities were passivated.

3:30 PM G5.7
PHOTOLUMINESCENCE UP TO 3.5 eV OF AMORPHOUS CARBON OXYNITRIDES A-CN_xO_y FILMS PREPARED BY A NITROGEN RADICAL SPUTTER METHOD. Yohko Naruse and Shoji Nitta, Dept. Electrical Engineering, Gifu University, Gifu, JAPAN.

Amorphous carbon nitride a-CN_x films prepared by a nitrogen radical sputter method show high photoconductivity, high resistivity, photoluminescence and electroluminescence. A-CN_x treated by the hydrogen plasma treatment show better electronic properties. In this paper, we have tried the oxygen plasma treatment for a-CN_x to get good electronic properties. A-CN_x prepared by a nitrogen radical sputter method is treated by an oxygen plasma forming amorphous oxynitrides a-CN_xO_y films. Photoluminescence PL spectra are observed in both of a-CN_x and a-CN_xO_y using the excitation by the He-Cd laser (325 nm). Comparing the both spectra, the intensity of PL in the ultraviolet region between $3 \sim 3.5$ eV of a-CN_xO_y is 2 to 3 times larger than that for a-CN_x, depending on the preparation conditions. Three effects of oxygen plasma treatment can explain the increase of photoluminescence at ultraviolet region: One is an increase of band gap with oxygen plasma treatment by the inclusion of oxygen into a-CN_x. The band gap E_o obtained by a Tauc'plot and that of E_{o4} obtained at the absorption coefficient α at 10000 cm^{-1} about 2 eV for a-CN_x and 2.7 eV for a-CN_xO_y are corresponding to nitrogen lone pair valence band to π^* antibonding conduction band. The band gap E_t between nitrogen lone pair to σ^* band for a-CN_x about 3.5 eV increases to 4.1 eV for a-CN_xO_y. The other two, the etching with oxygen plasma and the termination of pair defects by an oxygen atom, decrease both the defect localized electronic states in a-CN_xO_y and also the Urbach tail energy E_u forming the sharpness of the conduction band edge.

3:45 PM G5.8
SYNTHESIS AND CHARACTERIZATION OF ZINC GALLIUM OXYSULFIDES BLUE PHOSPHOR. J.S. Kim, Kim Kwangcheul, Hong Lee Park, Yonsei Univ, Institute of Physics & Applied Physics, Seoul, KOREA.

Synthesis of zinc gallium oxysulfides have been made for the first time and series of experiments have been done in order to reveal the pertinent characteristics , i.e, color purity, solid solubility, luminescence brightness and chemical stability. X-ray photoelectron spectroscopy (XPS), X-ray diffractometer (XRD), Cathdoluminescence (CL) and Energy dissipative spectroscopy (EDS) measurements have been employed to obtain the above mentioned characteristics.

4:00 PM G5.9
AN INVESTIGATION OF THE LUMINESCENCE IN AMORPHOUS EUROPIUM OXIDE - TITANIA SYSTEMS. James Ovenstone, Philip J. Titler, Robert Withnall and Jack Silver, University of Greenwich, School of Chemical and Life Sciences, London, UNITED KINGDOM.

A range of amorphous europium oxide - titania phosphors with the formula $Ti_{1-3x}Eu_{4x}O_2$, x varying between 0.000397 (Ti : Eu ratio = 360 : 1) and 0.143 (Ti : Eu ratio = 1 : 1). have been prepared and the luminescent properties investigated. These materials are the first reported inorganic, amorphous powder phosphors. We have shown that the emission brightness increases linearly with europium concentration up to a concentration of x = 0.0159. Beyond this concentration, brightness decreases to a europium concentration of x = 0.0238 then again continues to increase with europium

concentration, although the relationship is no longer linear. A Raman spectrometer has been used to investigate the changes in luminescence by exciting the material using radiation of wavelength equal to 632.8 nm HeNe laser. The luminescence has been investigated both in the Stokes and Anti-Stokes regions of the spectrum. The down conversion results clearly show an increase in the brightness of the phosphor up to a concentration of x = 0.0159 before quenching begins to occur and emission peak intensity falls. Similar behaviour can be observed in the up-conversion spectra, where again quenching is observed at concentrations greater than x = 0.0159. The peak positions do not change, however, and the relative peak intensities remain constant. The peak positions are quite distinct from those of both europium oxide and precipitated europium nitrate (the starting materials). In contrast, the Raman bands (Stokes and Anti-Stokes) themselves begin to exhibit some broadening as the concentration of europium reaches x = 0.0119, since they begin to approach the shape of the bands for precipitated europium nitrate (the starting material).

4:15 PM G5.10
FABRICATION AND CHARACTERIZATION OF THIN-FILM PHOSPHOR COMBINATORIAL LIBRARIE. Zhengwu Jin, Y. Yamada, T. Fukumura, M. Kawasaki, H. Koinuma, Tokyo Institute of Technology, Dept of Innovative and Engineered Materials, Yokohama, JAPAN; A.G. Umnov, V.Z. Mordkovich, International Center for Materials Research, Kawasaki, JAPAN.

It was demonstrated in our earlier work [1] that integrated materials libraries having different dopants in different concentrations can be manufactured by combining laser molecular beam epitaxy (laser MBE) with a masking system. In this work the laser MBE method was employed to fabricate thin-film libraries of ZnO-based phosphors on different substrates such as ITO/glass, sapphire and Pt/silicon. In particular, the libraries of Eu-doped ZnO were studied. Photoluminescence and low-voltage cathodoluminescence were measured through the pixels of different composition. The influence of heat treatment in oxidizing/reducing atmosphere was investigated. Substantial red cathodoluminescence was observed in a broad range of Eu concentrations. However, no photoluminescence was registered which is in good agreement with early observations by Hayashi et al. [2]. 1. Y. Matsumoto, M. Murakami, Zhengwu Jin, A. Ohtotomo, Mikk Lippmaa, M. Kawasaki, H. Koinuma, Jpn J. Appl. Phys., 38 (1999) L603 2. Y. Hayashi, H. Narahara, T. Uchida, T. Noguchi, Jpn J. Appl. Phys., 34 (1995) 1878

4:30 PM G5.11
ROOM-TEMPERATURE BLUE PHOTOLUMINISCENCE OF AlN FILMS, PREPARED BY RF MAGNETRON SPUTTERING. V. Ligatchev, S.F. Yoon, J. Ahn, Q. Zhang, Rusli, S. Zhgoon.

Two series of aluminium nitride (AlN) films are obtained by RF (13.56 MHz, 300 W) magnetron sputtering of pure Al target in argon (Ar) and nitrogen-hydrogen (N_2-H_2) mixture. For an 'a' series nominal substrate temperature (T_s) of 275°C and Ar flow rate (FR, 20 sccm) are invariable whereas the N_2-H_2 mixture (N_2:H_2=95:5) FR varied in 4 - 40 sccm range. For the 'b' series the Ar and N_2 H_2 flow rates are equal of 10 and 5 sccm (respectively), N_2:H_2=80:20, the T_s value is changed in 600 - 900°C range. Nominally undoped < 110 > oriented silicon plates are used as substrates. Near UV laser light beam (361 nm wavelength, 40±2 mW) have been used for the AlN photoluminescence (PL) excitation at the room temperature (293 K). The PL spectra contain main peaks with maximums at wavelengths of 420 - 440 nm for the all samples of the 'b' series and for a part of samples from the 'a' series, deposited at N_2-H_2 FR values below 25 sccm. The PL peaks maximum position for the residual samples from the 'a' series is in the 450 - 510 nm wavelength range. The typical peaks width is of 20 - 50 nm for the all AlN films. The residual samples PL intensity approximately 3 times lower than the similar values of the 'a' series films, deposited at the FR values below 25 sccm. The PL signal of the 'b' series samples is higher then the signal from any sample of the 'a' series. For the 'b' series, blue PL output enhanced more than ten times by the deposition temperature rising from 600 to 900°C. The results are analysed on the base of density of states deconvolution data [1] for these AlN samples. [1] V. Ligatchev, S.F. Yoon, J. Ahn, Q. Zhang, Rusli, S. Zhgoon, K.L. Chew. To be published in 'Diamond and related materials'.

SESSION G6: QUANTUM WELLS & QUANTUM DOTS
Chair: Markus Haase
Thursday Morning, April 19, 2001
Franciscan II (Argent)

8:30 AM G6.1
NANOCRYSTAL QUANTUM DOTS: BUILDING BLOCKS FOR TUNABLE OPTICAL AMPLIFIERS AND LASERS. Jennifer A. Hollingsworth, Alexander A. Mikhailovsky, Anton Malko, Victor I. Klimov, Los Alamos National Laboratory, Physical Chemistry and Applied Spectroscopy, Los Alamos, NM; Catherine A. Leatherdale, Hans -J. Eisler, Moungi G. Bawendi, MIT, Dept of Chemistry and Center for MS&E, Cambridge, MA.

We report bottom-up assembly of semiconductor nanocrystal quantum dots (NQDs) into solid-state devices for application in lasing and optical amplification. The building block NQDs range in size from 2 - 8 nm in diameter and, due to strong quantum confinement, exhibit size-dependent spectral tunability over an energy range as wide as several hundred meV. Further, NQDs of various compositions (e.g., PbS, InAs, InP, ZnS) can be prepared using relatively simple colloidal methods inspired by the solution-based organometallic reactions originally developed for the Cd chalcogenides, CdS, CdSe and CdTe [J. Am. Chem. Soc. 115, 8706 (1993)]. These colloidal routes yield freestanding QDs whose chemical reactivity and solubility are controlled by an organic ligand "cap" that is easily modified using simple surface-exchange reactions. NQDs can, therefore, be treated as large molecules in self-assembly-based processing of lasing and other optical materials. By utilizing NQDs of different sizes and compositions, facile manipulation of the spectral position of the optical gain from the far IR to the near UV is possible. We show that, in contrast to solutions of NQDs and assemblages of NQDs in glasses, close-packed films of CdSe NQDs exhibit narrowband stimulated emission [Science 290, 314 (2000)]. The stimulated emission is obtained both at low temperature and at room temperature, and its color is tunable with dot size. Moreover, the NQD films can be incorporated into microcavities of different geometries (micro-spheres, wires, tubes) that produce lasing in whisper gallery modes. The facile preparation, chemical flexibility, and wide-range spectral tunability due to strong quantum confinement are the key advantages associated with chemically synthesized NQDs.

8:45 AM G6.2
STUDY ON InAs/InP QUANTUM DOTS BY SYNCHROTRON RADIATION X-RAY DIFFRACTION AND PHOTOEMISSION SPECTROSCOPY. Ki Hong Kim, Dept of MS&E, Pohang University of Science and Technology (POSTECH), Pohang, KOREA; Sukho Yoon, School of MS&E and ISRC, Seoul National University, Seoul, KOREA; Jong Gyu Kim, Ho Won Jang, Kwang Ho Lee, Yang Mo Koo, Dept of MS&E, Pohang University of Science and Technology (POSTECH), Pohang, KOREA; Euijoon Yoon, School of MS&E and ISRC, Seoul National University, Seoul, KOREA; Jong-Lam Lee, Dept of MS&E, Pohang University of Science and Technology (POSTECH), Pohang, KOREA.

Extensive research has been made to fabricate self-assembled quantum dots (SAQDs) induced by lattice mismatch between the film and the substrate. The InAs SAQDs on the InP have wavelengths between 1.3 and 1.5 um, which are applicable to opto-electronic device for optical communications. The excess InAs and the aspect ratio(height and lateral size) of SAQD increased with temperature and V/III ratio, strongly suggesting that As/P exchange reaction at the surface played an important role in the SAQD formation. The local variation in the strain field around the dots may makr the As/P exchange reaction more complicated. However no reports on the effect of strain at InAs/InP interface on the change of Fermi level were studied. InAs self-assembled quantum dots(SAQDs) were grown on InP at various temperature and V/III ratios by metalorganic vapor deposition. The density, size, distribution, and shape of the InAs SAQDs were controlled by changing growth temperature and V/III ratio. Three sets of sample were prepared, with different dot size and density. In the two SAQDs samples, the InAs coverage was varied from 1 to 2 monolayer. The third is InAs island growth sample. The strain and atomic bonding status of SAQDs were respectively by synchrotron radiation x-ray diffraction and photoemission spectroscopy. The binding energy of As 3d weas decreased with the change of InAs coverage. As the increase of InAs coverage, the intensity of P 2p was decreased but the intensity of As 3d was increased. This provides evidence that strain increases the band bending in InAs SAQDs. The strain status of SAQDs samples was observed by reciprocal space mapping method. From these results, SAQDs formation mechanism will be discussed.

9:00 AM G6.3
EXCITED STATE RELAXATION MECHANISMS IN InP COLLOIDAL QUANTUM DOTS. Garry Rumbles, Don Selmarten, Randy E. Ellingson, Jeff Blackburn, Pingrong Yu, Barton B. Smith, Olga I. Micic and Arthur J. Nozik, NREL, Golden, CO.

We report some recent results on size-selected, colloidal quantum dots of InP prepared via controlled nucleation growth techniques. Using transient absorption and photoluminescence spectroscopy we have examined the roles of surface capping groups, etching procedures, excitation densities and temperature on the rates of carrier cooling and excited-state deactivation mechanisms. Samples have been

studied as colloidal suspensions and thin films. We also report findings on the role of mid-bandgap states that lead to anti-Stokes luminescence. Unlike CdSe, InP quantum dots are more difficult to synthesize, but offer an alternative direct bandgap material to study from the III-V class of semi-conductors. Our results will be compared to those reported for CdSe quantum dots prepared by similar procedures and the important differences and similarities between these two nanoparticle systems will be discussed.

9:15 AM G6.4
PHOTON-INDUCED CARRIERS TRANSFER FROM WETTING LAYER TO Ge QUANTUM DOTS GROWN ON Si(001). J. Wan, G.L. Jin, Y.H. Luo, Z.M. Jiang, J.L. Liu, and Kang L. Wang, Device Research Lab., Electrical Engineering Dept., University of California at Los Angeles, Los Angeles, CA.

Self-assembled Ge quantum dots grown on Si substrates have been an area of recent intense study. Many studies have been done on the growth mechanism, electrical and optical properties of Ge quantum dots. Although photoluminescence from quantum Ge dots has also been widely studied, little has been done on the correlation between PLs from the quantum dots and the wetting layers. In this work, temperature and excitation power dependent photoluminescence measurements were carried out for the multi-layer structure of Ge quantum dots grown on Si(001) substrate grown by gas source molecular beam epitaxy. When the excitation power incresed from 10 mW to 400 mW, the photoluminescence peak from Ge quantum dots showed a large blueshift of 34 meV while that of wetting layers did not shift. These two different power dependence behaviors are explained in terms of the type-II and type-I band alignments for the quantum dots and the wetting layers, respectively. When the measuring temperature increased from 8 to 20K, an anomalous increase of photoluminescence intensity from quantum dots was accompanied by a rapid decrease of that from the wetting layers. This implyied that a large portion of photon-induced carriers in the wetting layer was transfered to the neighboring dots and Si layer, thus resulting an increase of photoluminescence intensity of quantum dots.

9:30 AM G6.5
LOW PRESSURE PHASE TRANSITIONS IN WURTZITE CdSe QUANTUM DOTS. Robert W. Meulenberg and Geoffrey F. Strouse, Department of Chemistry, University of California, Santa Barbara, CA.

Over the last several years, significant efforts in understanding the effects of high pressures on quantum dots (QDs) have been reported. It has been shown that the high-pressure phase transition from wurtzite (WZ) to rock-salt for CdSe QDs is doubled (3 - 6 GPa), but the energy dependence of the absorption edge is near that of the bulk value ($\partial E/\partial P \sim 45$ meV/GPa). Upon release of pressure, mixtures of both hexagonal and cubic (WZ and zinc blende (ZB), respectively) structures are seen, due to the low energy of interconversion of the lattice. Surprisingly, ZB is rarely observed for II-VI nanomaterials although it is thermodynamically preferred and moderate to low pressures should induce a WZ $\rightarrow$ ZB phase transition. Experiments with pressures in lower pressure ranges ($<$ 1 GPa) have been ignored and may give insight into these types of low energy phase transitions. We report findings of QD size dependent pressure coefficients and postulate that changes in the band structure of quantum confined semiconductors (which lead to these changes in the pressure coefficient) are a function of the compressibility and defect nature of the material, which induce surface reconstruction events. We present optical absorption and photoluminescence data, as well as time-revolved luminescence data to infer to the mechanism of the pressure dependence.

9:45 AM G6.6
EFFECT OF RAPID THERMAL ANNEALING ON THE PHOTOLUMINESCENCE AND STRUCTURE PROPERTIES OF InGaN QUANTUM DOTS. Chua Soo Jin, Zhang Ji, National University of Singapore, Dept of Electrical and Computer Engineering, SINGAPORE; Hao Maosheng, Institute of Material Research and Engineering, SINGAPORE; Li Peng, National University of Singapore, Dept of Electrical and Computer Engineering, SINGAPORE; Sun Wenhong, Institute of Material Research and Engineering, SINGAPORE.

The InGaN alloys have been used as active layers of InGaN-based blue and green light emitting diodes (LEDs) and laser diodes (LDs). However, it is generally the InGaN quantum dots (QDs), instead of InGaN quantum well (QW), that plays the crucial role. Since the InGaN QDs are generally deposited at relative low growth temperature followed by growing other layers at high growth temperature for practical InGaN-based LEDs and LDs, it is concerned on the thermal stability of QDs at high growth temperature. We report the effect of post-growth rapid thermal annealing (RTA) process on the photoluminescence and structure properties of InGaN QDs in the InGaN/GaN single quantum well (SQW). The InGaN/GaN SQW sample was grown by MOCVD: firstly 20nm nucleation GaN layer was deposited on sapphire at 530°C, followed by 2um undoped GaN layer at 1050°C; then SQW with QDs was grown at 760°C; finally SQW was capped with 30nm GaN layer at 1050°C. The as-grown sample was divided small pieces; and two pieces with same room temperature photoluminescence (PL) properties were chosen to be thermal annealed at 1100°C and 1000°C, 50°C higher and lower than the growth temperature of cap layer for 15 seconds in N2 ambient, respectively. The room temperature PL results showed that 1100°C RTA had much greater effects on InGaN QDs. The PL intensity enhanced by one order and wavelength blue-shifted almost 30nm after 1100°C RTA. While neither the intensity nor wavelength of room temperature PL changed much for 1000°C RTA sample. This suggests that the InGaN QDs deposited at relative low temperature may be changed both on size and composition during the following structure growth at high temperature. This effect may be depressed by deposition an AlGaN stop-layer at low temperature. The microstructure of QDs after RTA is being investigated by TEM.

10:30 AM G6.7
CHEMICAL MAPPING AND PHOTOLUMINESCENCE OF InGaN/GaN LEDS. Nikhil Sharma, Menno Kappers, Jonathon Barnard, Mary Vickers and Colin Humphreys, Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UNITED KINGDOM.

Optimisation of InGaN/GaN multiple quantum well (MQW) light emitting diodes (LEDs) using conventional characterisation techniques has led to a marked improvement in their performance. However conventional quantitative techniques such as x-ray diffraction are effected by residual strain in the layer and cannot easily measure the variation of indium concentration from well-to-well, which effects the light emission of the LED. Hence we have developed a technique of energy filtering inelastically scattered electrons in a transmission electron microscope (EFTEM) from gallium, nitrogen, and indium. The images are made quantitative by comparing the InGaN signal with the bulk GaN signal, giving a 3% standard error from the mean indium concentration. Hence we have formed high resolution (1nm) cross-sectional quantitative maps of the MQW, which are largely independent of strain in the layer. Using a combination of EFTEM and annular dark field imaging in the TEM, we have shown that edge type dislocations disrupt the MQWs to form V-defects (20nm diameter) [1]. Chemical mapping of V-defects shows a pyramidal volume of GaN in the MQW, which leads to an unwanted broadband 438 nm emission in the photoluminescence spectra [2]. This paper will show that routine characterisation using a comparison of EFTEM, high-resolution x-ray diffraction and photoluminescence leads to an improved growth recipe for both MOCVD and MBE grown MQWs. We will show that the brightest light emitting quantum wells are 2 to 4 nm wide, have a very flat morphology and a uniform indium concentration from well-to-well. [1] N. Sharma, P.J. Thomas, D.M. Tricker and C.J. Humphreys, APL, 77 (9), p.1274, 2000 [2] X.H. Wu, C.R. Elsass, A. Abare, M. Mack, S. Keller, P.M. Petroff, S.P. DenBaars, and J.S. Speck, Appl. Phys. Lett. 72 (6), p.692, 1998

10:45 AM G6.8
LUMINESCENCE CHARACTERISTICS OF InGaN-InP QUANTUM WELL STRUCTURES BY IMPURITY-FREE VACANCY DISORDERING. J. Zhao, Nat Univ of Singapore, Dept Mat Sci, Singapore & Tianjin Normal Univ, Dept Physics, PR CHINA; Z.C. Feng, Institute of Materials Research & Engineering, SINGAPORE; J.C. Deng, Nat Univ of Singapore, Dept Mat Sci; G. Xu, Nat Univ of Singapore, Dept Mat Sci & McMaster Univ, CANADA; S.J. Chua, Inst of MS&E, SINGAPORE.

In fabricating luminescence devices for integrated optoelectronic and photonic application, InGaAs-InP multiple quantum wells (MQWs) structures have attracted research interests. Post-tuning of optical band gap energy can be achieved from these MQW structures, which possess the advantage to avoid the complicated post growth processing. Several technical approaches have been explored to achieve this purpose, among which impurity-free vacancy disordering (IFVD) technique shows more promising because it can keep high crystal quality and low optical propagation loses as well as does not introduce free-carrier concentration. IFVD, utilizing a dielectric layer as Ga sink at elevated temperature, could result in the redistribution of Ga vacancies in MQW structures to enhance quantum wells intermixing and thus to enhance the luminescence. We have also employed SiO_2 and Si_3N_4 as well as spin on glass (SOG) as dielectric layer in IFVD of InGaAs/InP system, for the first time. In this paper, a systematic investigation on luminescent characteristics of InGaAs/InP MQW system using SiO, SiN and SOG as dielectric layers in IFVD is reported. Photoluminescence (PL) was measured by a Fourier transform near infrared (NIR) PL system at a varied temperature range of 10-300 K. Band gap blue shift of InGaAs/InP MQW structures by IFVD was found to vary with different dielectric

layers and depend on the annealing temperature. These are due to the mechanism of quantum well intermixing, which was confirmed through the corresponding secondary ion mass spectroscopy (SIMS) measurements. Our results also show that the dielectric capped layer and rapid thermal annealing (RTA) could cause the quantum wells intermixing which results in the band gap blue shift. Optimum condition can be reached by suitable dielectric choice and annealing condition.

11:00 AM G6.9
InGaAs-InP QUANTUM WIRE STARK EFFECT MODULATORS: EFFECT OF WIRE WIDTH IN THE OPTIMIZATION OF CHANGES IN EXCITONIC ABSORPTION AND INDEX OF REFRACTION. M. Xu[a] and W. Huang, Electrical Engineering and Computer Science Department United State Military Academy, West Point, NY. ([a]Current address: Microsoft Corp., Bellevue, WA); F. Jain, Department of Electrical and Computer Engineering, University of Connecticut, Storrs, CT.

Quantum wire/dot modulators offer superior performance over their quantum well counterpart due to enhanced excitonic binding energy. This paper presents simulations on InGaAs-InP quantum wire Stark effect optical modulators showing a novel trend. While the excitonic binding energies and absorption coefficients increase as the width of the wire is decreased, the refractive index change Δ n is maximized at a wire width depending on the magnitude of the applied electric field. For example, Δ n is maximized at a width of about 100Å for an external electric field of 120kV/cm in an InGaAs quantum wire. This behavior is explained by considering the opposing effects of the binding energy and the electric field on the electron-hole overlap function as the wire dimensions are reduced. Practical InGaAs-InP modulators using V-groove structures are also presented.

SESSION G7: DEVICES AND DEVICE APPLICATIONS
Chair: Thomas E. Felter
Thursday Afternoon, April 19, 2001
Franciscan II (Argent)

1:30 PM *G7.1
COLOR CENTERS IN MAGNESIUM DOPED POLYCRYSTALLINE ALUMINA. L.R. Brock, K.C. Mishra, M. Raukas, W. Lapatovich and G. Wei, Research and Development, OSRAM Sylvania Inc., Beverly, MA.

We have investigated color centers in magnesium doped polycrystalline alumina (PCA) using absorption, excitation, and emission spectroscopy. Most of the color centers that were reported in earlier studies of the crystalline material have been observed to be present in the polycrystalline material.[1] The absorption spectral features observed in the PCA are attributed to various color centers; however, they are not sufficiently resolved to make unique assignments. Suitable combinations of excitation and emission spectroscopy and also measurements at low temperature were therefore used to identify most of the color centers in this material. Among the numerous color centers that we have identified in PCA are variations of electron centers including F, F^+, F_2, F_2^+, F_2^{2+}, and F^+-Mg ($(V_o^o\text{-}Mg_{Al})^x$). The most prominent oxygen vacancy related defect observed at room temperature was the F^+-Mg center, with absorption bands located at 217 and 247 nm, and an emission band at 310 nm. This center can be thought of as being formed by association of an F^+ center with a Mg defect. The single crystal sapphire samples containing no Mg show only F^+ (V_o^o) centers with 230 and 257 nm absorption bands, and a 328 nm emission band. Additionally, low temperature (22 K) fluorescence measurements of PCA led to emission from F_2^{2+} center at 467 nm. The observed 368 nm fluorescence peak could possibly be attributed to the zero-phonon line associated with the F_2^+ center.
[1]For example, see G.J. Pogatshnik, Y. Chen and B.D. Evans, IEEE Trans. Nucl. Sci. NS-34 (1987) 1709, and references therein.

2:00 PM G7.2
THE EFFECT OF RESIDUAL GASES ON THE DEGRADATION OF SULFIDE BASED PHOSPHORS. Michael Ollinger, Valentin Craciun and Rajiv K. Singh, Univ of Florida, Dept of MS&E, Gainesville, FL.

Sulfide based phosphor materials have been routinely utilized in cathode ray tube displays (CRT), electroluminescent (EL) displays, and have been explored for field emission display (FED) applications due to their high luminescent efficiencies in comparison to oxide based phosphors. However, the sulfide-based phosphors are prone to degradation of the cathodoluminescent properties caused by the interaction of the e-beam with the adsorbed residual gases on the particle surface of the phosphors. A complete understanding of the mechanism taking place has not been achieved to date. To overcome this critical issue we have synthesized nanofunctionalized phosphor powders, which are formed by coating a very thin film onto the surfaces of the phosphor powders using a novel atomic flux coating technique and degraded in vacuum dominated by the presence of various background gases such as: hydrogen, oxygen, water, and methane. The coating technique uses a 248 nm wavelength excimer laser, with a pulse duration of 25 ns operated from 5-15 Hz at energies between 2-5 J/cm^2, which strikes a solid target under a high vacuum (10^{-5} Torr) and creates a plume of atomic species. These species or nanoclusters are then deposited onto the host phosphor particles that are being mechanically agitated during deposition for coating uniformity. Characterization of the brightness and degradation was performed using cathodoluminescence (CL). The stoichiometry and chemical composition of the particle surface was studied using x-ray photoelectron spectroscopy (XPS). The presence of the coating was seen using Auger Electron Microscopy (AES), and the surface changes before and after degradation using a Field Emission Scanning Electron Microscope. The effect of the coatings on the degradation characteristics of Y_2O_2S:Eu has been investigated and degradation mechanisms for the various background gases has been proposed.

2:15 PM G7.3
EXCITED STATE ACTIVATOR INTERACTIONS AND THEIR EFFECT ON CATHODOLUMINESCENCE EMISSION EFFICIENCY AT LOW ELECTRON BEAM ENERGIES. C.H. Seager and D.R. Tallant, Sandia National Laboratories, Albuquerque, NM.

The design of Field Emission Displays is severely constrained by the universally poor cathodoluminescence (CL) efficiency of most phosphors at low excitation energies. We have previously reported spectrally-resolved, pulsed CL and photoluminescence (PL) decay in several phosphors activated by rare earth and transition metal impurities, including Y_2O_3:Eu, Y_2SiO_5:Tb, and Zn_2SiO_4:Mn. At short times after the cessation of excitation these decay curves display non-first order behavior, particularly at high activator concentrations and low electron beam energies. These peculiar decay curves are also seen in all of these phosphors under high intensity photon excitation and appear to associated with the interaction of excited activator states. Correlated with these effects is a worsening of the electron beam energy dependence of CL efficiencies at higher activator densities. This correlation demonstrates that the beam-voltage-induced variation of radiative efficiency that we see in pulsed decay studies of a single luminescent transition are magnified to much more serious effects on the total steady state radiative CL efficiency. It also demonstrates that non-radiative losses before activator excitation could well be less important to the low-voltage CL efficiency problem than those which occur after energy is transferred to the activator population. In addition, it focuses attention on the high excitation density feature of low energy electron excitation rather than the quality of the lattice near surfaces of phosphor particles. In this talk we will present new CL and PL data, reduced in such a fashion that the interesting transitions from conventional 1st order decay processes to 2nd order behavior are apparent. We will also discuss CL efficiency and decay data obtained at cryogenic temperatures, where the effect of restricted phonon creation rates impacts non-radiative decay most strongly. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

2:30 PM G7.4
LONG-TERM CATHODOLUMINESCENT CHARACTERIZATION OF THIN-FILM OXIDE PHOSPHORS IN A WIDE RANGE OF ELECTRON EXCITATION DENSITIES. V. Bondar, Lviv National University, Department of Physics, Lviv, UKRAINE; T. Felter, Lawrence Livermore National Laboratory, Livermore, CA; C. Hunt, University of California at Davis, Department of Electrical and Computer Engineering, Davis, CA; Yu. Dubov, Lviv National University; A. Chakhovskoi, University of California at Davis, Dept of ECE, Davis, CA.

Long-term measurements of cathodoluminescence (CL) of thin film oxide phosphors Zn2SiO4:Ti, Y2SiO5:Ce (blue), Zn2SiO4:Mn, ZnGe2O4-Mn (green), Y2O3:Eu, (ZnGd)2O3-Eu (red) have been made in the range of electron excitation power densities from 0.1 to 20 W/cm2. The measurements were made in the laboratory-made CRT prototype with simultaneous registration of CL intensity, electron beam current and energy. It was found that at e-beam power densities less than 0.5 W/cm2 most of the oxide films did not show substantial decrease of CL intensity within measurement accuracy, 3-5%. The intensity was found to decrease at power densities greater than 1W/cm2. The decrease follows a $(I0/I\text{-}1) = K*t^{1/2}$ dependence, which suggests thermal diffusion to be the mechanisim for CL intensity decrease. The long-term behavior of the blue thin film phosphor Zn2SiO4:Ti in the range of 1-20 W/cm2 is somewhat different depending on power densities, excitation energies and current densities. Two constituents of CL intensity loss have been

revealed in Zn2SiO4:Ti films. At low electron energies (2 keV) the decrease of CL of Zn2SiO4:Ti films at power densities 1-10 W/cm2 is monotonic with K= 0.01-0.1, depending on current density. At higher energies (2.5-3.5 keV) or power densities a sharp decrease is observed initially with K=0.2 - 0.4 and a slow decrease with K=0.01-0.06 - during longer times of irradiation. At higher e-beam power density, the behavior is more extreme. This behavior suggests the presence of two concurrent processes during e-beam excitation: thermal diffusion, which results in the decrease of CL intensity and a recombination process, which results in thermal stabilization of emission. The results obtained are discussed in terms of a recharging model of luminescence centers Ti3+ in Zn2SiO4:Ti with creation of deeper levels resulting in changes (improvement) of temperature stability parameters of thermal activation of emission centers and an increase in phosphor temperature stability.

2:45 PM G7.5
OPTICAL AND ELECTRICAL PROPERTIES OF CR-SiO THIN FILMS FOR FLAT PANEL DISPLAYS. Richard Wood, Peter Hofstra, David Johnson, Luxell Technologies Inc., Mississauga, ON, CANADA.

Low temperature fabrication of transparent conducing materials is a key issue in flat panel display production. Though Cr-SiO cermet thin films have previously been used only as thin film resistors in a variety of microelectronics applications, it is shown in this paper that the material can successfully be used as a transparent to semi-transparent conductor in some applications if the value of the extinction coefficient, k, can be kept low. Thus a detailed study of the interdependence of the resistivity and optical properties of Cr-SiO is presented for the first time within the context of its use in the flat panel display industry. Electron-beam deposition is used to uniformly deposit the material over areas commensurate with medium to large flat panel displays (up to a 4 foot diameter). Various techniques, including ellipsometry and reflectometry, are used to characterize the index of refraction, n, and the absorption constant, k over optical wavelengths 400-1000 nm. It is shown how these properties, as well as resistivity of the films, vary with deposition conditions as well as the Cr/Si ratio of the source material. A correlation is demonstrated between the resistivity of the film and the absorption constant, k. Scanning electron microscopy is used to demonstrate the crystallinity of the films, while X-ray photoelectron spectroscopy (XPS) is used to examine bonding states. Finally it is shown how these films can be used successfully as transparent conductors in the production of thin film electroluminescent (TFEL) and organic light emitting diode (OLED) flat panel displays. Specifically, Cr-SiO can be employed as part of Luxell's optical interference structure, known as the Black Layer, used to increase contrast in TFEL and OLED displays.

3:00 PM G7.6
LOW-TEMPERATURE TECHNOLOGY AND PHYSICAL PROCESSES IN GREEN THIN-FILM PHOSPHOR Zn_2GeO_4-Mn. V. Bondar, S. Popovich, Lviv National University, Department of Physics, Lviv, UKRAINE; T. Felter, Lawrence Livermore National Laboratory, Livermore, CA; J. Wager, Department of Electrical and Computer Engineering, Oregon State University, Corvallis, OR.

The efficient and stable green thin-film phosphor Zn_2GeO_4:Mn for field emission displays has been developed. Unlike other oxide phosphors this material has low crystallization temperature, which is compatible with industrial technologies and therefore may replace the less stable sulfide phosphors. Thin film Zn_2GeO_4:Mn phosphors were synthesized by a modified RF-sputtering method and thermal crystallization. The dependence of luminescent intensity on concentration was investigated and the optimal Mn_2 content was determined. Based on X-ray and luminescence analyses the most efficient crystallization temperature was determined. It was found that luminous efficiency of Zn_2GeO_4:Mn films is determined by deposition and annealing temperature as well as by sputtering gas (oxygen content). ESR spectra of Zn_2GeO_4:Mn show two types of lines: a broad one (DHpp@800 G) with geff = 2.0, that may be interpreted as unresolved fine structure (FS) of the ESR spectrum in the disordered systems from isolated ions Mn2 (6S5/2, 3d5), and a series of about 30 narrow lines that may be interpreted as allowed and forbidden transitions of the fine structure (FS) central component of isolated Mn_2 ions. The temperature dependence of luminescence of Zn_2GeO_4:Mn is characterized by thermal quenching of emission at temperatures above 200C with activation energies of quenching 0.45 eV in a region of 200-350C. Based on photoexcitation and photoconductivity spectra, their temperature dependencies, as well as thermostimulated luminescence, the recombination mechanism of excitation was found to be responsible for the intracenter emission of manganese centers in Zn_2GeO_4:Mn. For field emission display applications thin films Zn_2GeO_4:Mn with color coordinates (CIEx = 0.302, CIEy = 0.668) and efficiency of 2.4 lm/W under 2 keV electron excitation have been created.

3:45 PM *G7.7
RECENT PROGRESS TOWARDS SOLID STATE LIGHTING. Gerd O. Mueller, Regina Mueller-Mach, LumiLeds Lighting, A Joint Venture of Agilent Technologies and Philips Lighting Advanced Laboratories, San Jose, CA.

Two essentials mark the progress towards solid state lighting: (1) the availability of Light Emitting Diodes (LED) of all colors, and (2) the availability of suitable phosphors for generating white light. These phosphors, now sometimes termed color converters, as they convert e.g. blue into yellow, or blue into red and green, need more research work to perfect them, but allow for rather applicable devices. Besides the material issues, design criteria will be discussed, and some predictions given.

4:15 PM G7.8
A NEW APPROACH TO PRODUCE LIGHT-EMITTING POROUS POLYCRYSTALLINE SILICON THIN FILMS. P.G. Han, H. Wong and H.P. Chan, City Univ of Hong Kong, Dept of Electronic Engineering, Kowloon Tong, HONG KONG; M.C. Poon, Hong Kong Univ of Sci. & Tech., Dept of Electrical & Electronic Engineering, Clearwater Bay, HONG KONG.

It has been realized that the instability and the low efficiency are the major constraints for the applications of light-emitting porous silicon (PS) in optoelectronics. Although a lot of efforts have been devoted for finding methods to prepare high quality PS films, aging induced degradation is still significant. In this work, we develop a novel method to prepare nano-scale porous structure. An oxide layer was first grown on a heavily doped polysilicon thin film then plasma etching was conducted to remove the oxide layer. As a result, without any masking and lithographic process, honeycomb shaped silicon pores were formed on the polysilicon layer. Atomic-force microscopy (AFM) and scanning electron microscopy (SEM) were performed to probe the surface morphology of the prepared porous films. Compared to the PS films prepared by anodization, a more efficient and more stable visible photoluminescence (PL) (in the range of 500 nm to 800 nm) was observed. Details of the dry etching process and process-dependent optical characteristics of the thin films are also given.

4:30 PM G7.9
FORMATION OF LUMINESCENT STRUCTURES ON CONVENTIONAL CZOCHRALSKI SILICON WAFERS BY PLASMA HYDROGENATION AND OXYDATION. Reinhart Job, Alexander G. Ulyashin, Wolfgang R. Fahrner, Univ of Hagen, Hagen, GERMANY.

In this work a study of light emitting layers, which were formed by hydrogen plasma treatments of monocrystalline silicon with following oxidation in air, flowing oxygen or oxygen plasma will be presented. The influences of the plasma parameters (plasma frequency, power, substrate temperature during the plasma hydrogenation, etc.) and of the parameters of the heat treatments for the oxidization (temperature, time, ambient) on the efficiency of the luminescence are studied. The hydrogenation was done in standard PECVD setup with 13.56 MHz and 110 MHz at about 250°C. The layers were analyzed by scanning electron microscopy, Raman and photoluminescence (PL) spectroscopy. Mechanical beveling of the samples was done in order to provide also depth resolved measurements. It was shown that in the visible spectral range light emission from thin nanostructured layers near the wafer surface can be observed after the oxidization of the hydrogen plasma treated samples. The evolution of Si-H and H-H bonds was measured in such layers by Raman spectroscopy. In addition the evolution of the PL intensities in the visible spectral range is also studied. It was found that the efficiency of such emission strongly depends from the time/temperature of the oxidization and from the initial structuring by the hydrogen plasma. It is assumed that the possible reason of the light emission is the formation of Si-O-H complexes. It can be concluded that the hydrogen plasma treatment with the following oxidization can be used for the formation of light emitting structures operating in the visible spectral range.

4:45 PM G7.10
STRONG ULTRA-VIOLET ELECTROLUMINESCENCE FROM POROUS SILICON LIGHT EMITTING DIODE. J. Yuan[a], H.L. Tam[a], K.F. Li[a], W.K. Wong[b] and K.W. Cheah[a]. [a]Department of Physics, Hong Kong Baptist University, Kowloon Tong, CHINA. [b]Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, CHINA.

Porous silicon light emitting diode was found to emit strong line shaped ultraviolet emissions under a forward bias driving voltage of about 20 volts. The intensity is sufficiently strong to pump an organic crystal, Tb-dipicolinic acid, producing clear Tb 4f intra-shell transition photoluminescence spectrum. Although an early report proposed that the emission is due to micro-plasma discharge of nitrogen gas trapped in the porous micro-cavities. Purging of the

device with various gases did not change the emission spectral characteristics. However, purging can quench the electroluminescence, which recovered its intensity partially after each purging, and the electroluminescence recovered completely overnight. The device also showed negative differential resistance in its current- voltage characteristics that is frequency dependent. Thus, this was attributed to breakdown in localized space charge, which can be reduced after surface passivation. From the results, the electroluminescence mechanism is tentatively attributed to core recombination in the porous layer and the spectrum characteristics is due to microcavity effect between the top Au contact and silicon substrate.