# SYMPOSIUM V

# Rare-Earth Doping for Optoelectronic Applications

March 29 - 31, 2005

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<sup>\*</sup> Invited paper

SESSION V1: RE Doping - Perspectives and Retrospectives

Chairs: Tom Gregorkiewicz and John Zavada Tuesday Morning, March 29, 2005 Room 2009 (Moscone West)

#### 8:30 AM <u>\*V1.1</u>

Erbium in Semiconductors: Where are we Coming From; Where are we Going? A. R. Peaker, The University of Manchester, School of Electrical Engineering & Electronics, Manchester, United Kingdom.

It is one of the curious twists of technology that transitions which are parity forbidden in the free ions of rare earths should have become of immense importance in solids used in fluorescent lighting, cathode ray tubes and optical amplifiers. It is not an unreasonable expectation that having achieved such success with excitation from photons and accelerated electrons that junction electroluminescence should also be important. Since Ennen demonstrated good low temperature electroluminescence in silicon in the early 80's, a formidable amount of work has been done to try to understand the excitation and quenching mechanisms in common semiconductor hosts such as silicon and gallium arsenide. Although some remarkable experimental results have been obtained for erbium in nanostructures, insulators and wide band-gap materials the performance in bulk silicon and silicon germanium is disappointing. More importantly we still have not achieved a comprehensive, detailed understanding of the processes of non-radiative competition to the rare earth emission. In this paper the key steps that have been made over the last twenty years towards our present day knowledge of erbium luminescence in semiconducting hosts are reviewed and an assessment made of what remains to be done.

## 9:00 AM <u>\*V1.2</u>

Microcavity-Controlled Radiation From Rare Earth Ions. Albert Polman, FOM-Institute AMOLF, Amsterdam, Netherlands.

Microcavities provide a photonic environment to rare earth ions that dramatically modifies their emission rate and emission spectrum. We first demonstrate this in toroidal optical microcavities that are doped with erbium by ion implantation. Cavity quality factors as high as  $10^8$ are achieved and as a consequence, the erbium emission splits up in a sharply peaked mode spectrum, with the modes separated by the cavity free spectral range. Using confocal optical microscopy, Er ions in particular sections of the cavity are selectively excited and different degrees of mode coupling can be spatially resolved. When pumped trough a tapered optical fiber at 1480 nm, these Er-doped microcavities show single-mode lasing at 1.5  $\mu m$  above a threshold pump power as low as 4  $\mu W$ . These data present the first erbium-doped microcavity laser on a silicon substrate that is fabricated entirely using CMOS technology. A model that describes the Er population dynamics in the cavity is presented, and very well describes the experimentally found dependence of lasing characteristics on Er concentration, pump power, and coupling conditions. Next, Er-doped toroidal microcavities were co-doped with Si nanocrystals that act as efficient sensitizers for Er. The Si nanocrystals cause significant scattering of the optical modes, but interestingly, over 99 % of the scattered light is preferentially coupled back into a cavity mode. We attribute this to a classical analogue of the Purcell effect, that relates the spontaneous emission rate (and as we now propose, also the scattering rate) to the final optical density of states. We also used one-dimensional Fabry-Perot microcavities to demonstrate a novel method to determine the optical absorption cross section spectrum of Er around 1.5  $\mu$ m, using ring-down spectroscopy. This technique enables accurate measurements in a thin-film geometry, i.e. without the need to fabricate waveguides, and can be applied to all rare earth ions. We find, contrary to earlier claims, that the intra-4f transition strength of Er<sup>3+</sup> is not affected by the presence of Si quantum dots that act as sensitizers for Er. Finally, we present data on controlled spontaneous emission of Er in photonic crystals. Er-doped nanocavities are made in two-dimensional SOI photonic crystal waveguides. Three-dimensional photonic crystals, doped with erbium, were made using colloidal self-assembly followed by infiltration with Si using CVD. The photonic crystals possess a full photonic band gap around 1.5  $\mu$ m. By varying pump wavelength and temperature, we are able to probe the effect of the local optical density of states on the emission from Er and Nd ions located at different symmetry locations in the photonic crystal.

## 9:30 AM <u>\*V1.3</u>

Light Emitting Devices based on Rare-Earth Doped Silicon Nanoclusters. Francesco Priolo<sup>1</sup>, Alessia Irrera<sup>2</sup>, Domenico Pacifici<sup>1</sup>, Giorgia Franzo<sup>1</sup>, Calogero Presti<sup>4</sup>, Fabio Iacona<sup>2</sup>, Delfo Sanfilippo<sup>3</sup>, Gianfranco Di Stefano<sup>3</sup> and Giorgio Fallica<sup>3</sup>; <sup>1</sup>Dept. Physics & Astronomy, MATIS-INFM & Univ. Catania, Catania, Italy; <sup>2</sup>IMM, CNR, Catania, Italy; <sup>3</sup>STMicroelectronics, Catania, Italy; <sup>4</sup>Scuola Superiore di Catania, Catania, Italy.

In the last decade, rare-earth doping of silicon nanoclusters has been proven to be one of the most promising method able to bypass the scarce light emission capabilities of silicon. It is nowadays ascertained that silicon nanoclusters are very efficient sensitizers for the Er luminescence at 1.54 micron. Indeed, each nanocluster absorbs the incoming photons with effective absorption cross section which are more than three orders of magnitude higher than for Er, and then rapidly transfers its energy to nearby Er ions, thus producing an emission of light at 1.54 micron which is two orders of magnitude more efficient than for Er in pure silica. Recently, higher quantum efficiencies have been obtained by incorporating in the film high concentrations of very small amorphous silicon clusters, thus demonstrating that amorphous, as well as crystalline, Si nanoclusters can be efficient sensitizers for the Er luminescence. A model based on an energy level scheme taking into account the coupling between each Si nanocluster and the neighboring Er ions will be reported. The role of Si nanoclusters and of strong gain limiting processes, such as cooperative up-conversion and confined carriers absorption from an excited nanocluster, in determining positive gain at 1.54 micron will be investigated in details, and the implications of the finite transfer time on the overall efficiency of the energy transfer mechanism will be discussed. Efficient room temperature light emission from electroluminescent devices based both on Er and Tm-doped Si nanoclusters has been demonstrated. It has been shown that the silicon nanoclusters dispersed in the active layer allows for a good current injection in the otherwise insulating matrix and determine an efficient excitation of the rare-earth. In particular, an effective excitation cross section of the order of 10-14 cm2, i.e. two orders of magnitude higher if compared to optical pumping, has been measured under electrical excitation. Due to the high excitation cross section and to the efficient current injection, internal quantum efficiencies of the order of 1% have been estimated. For application, we are mostly interested in the power efficiency of these devices. In order to increase the external efficiency, we coupled the emitting system with a 2D photonic crystal structure opportunely fabricated to efficiently couple the emitted radiation to the free space vertical modes, thus reducing the total internal reflection of the emitted light and increasing the overall emission yield. These data will be presented and future trends discussed.

# 10:30 AM extstyle\* extstyle\*

Laser Applications. Zakhary F. Krasilnik<sup>1</sup>, Boris Andreev<sup>1</sup>, Wolfgang Jantsch<sup>2</sup>, Denis Kryzhkov<sup>1</sup>, Viktor P. Kuznetsov<sup>1</sup>, Hanja Przybylinska<sup>3</sup>, Vyacheslav Shmagin<sup>1</sup>, Margarita Stepikhova<sup>1</sup>, Nguyen Quang Vinh<sup>4</sup> and Artem Yablonsky<sup>1</sup>; <sup>1</sup>Semiconductor Physics, Institute for Physics of Microstructures RAS, Nizhny Novgorod, Russian Federation; <sup>2</sup>Solid State Physics, Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, Linz, Austria; <sup>3</sup>Solid State Physics, Institute of Physics PAS, Warsaw, Poland; <sup>4</sup>Optoelectronics, Van der Waals - Zeeman Institute, University of Amsterdam, Amsterdam, Netherlands.

The research on Er-doped silicon continues to be spurred by the prospects for realization of silicon-based photonic components first of all efficient light-emitting diodes and lasers. In this contribution we describe an original method of sublimation MBE (SMBE) and show its capabilities for the growth of effective light-emitting Si:Er structures, in particular for the growth of a novel type of Er-doped structures - the multilayer Si/Si:Er/Si/Si:Er.../Si structures exhibiting superior luminescent properties. Results of high-resolution PL and magneto-optical spectroscopy studies performed for such kind of structures will be presented. It will be shown the ability to achieve in these structures the preferential formation of a single type of optically active Er-related centers, of the particular Er-1 center. We identify the orthorhombic-I symmetry of the Er-1 center. High concentration of this specific center (up to 32% from the total amount of Er impurity) was found in Si:Er multilayer structures. The ultra-narrow linewidth (<10?eV) being characteristic for Er-1 center emission indicates a possibility for a 103-104 increase of the expected gain coefficient in multilayer Si:Er structures. Therefore, these structures emerge as the plausible candidates for achieving population inversion and stimulated emission in Si based materials. The gain factor accessible in Si:Er SMBE structures is estimated as 3-30 cm-1. The results of simulations for the parameters of real laser-type structures and the principles for their realization will be discussed. Electroluminescence in SMBE light emitting diodes is observed both in the forward and reverse bias regimes. LEDs emit at the breakdown conditions up to room temperature. The influence of the breakdown origin (avalanche or tunneling) on the intensity and excitation efficiency of Er-related EL is investigated. It has been shown that the LEDs operating under mixed breakdown conditions are most preferential. New results on the EL behavior in diode structures with the active Er doped layers specifically positioned relative to the p-n-junction will be presented. The work was partially supported by the RFBR (grants #04-02-17120, #04-02-08240ofi-a) and INTAS

(grant #03-51-6486) foundations.

#### 11:00 AM V1.5

Multistep Resonant Excitation of Erbium Ions in Thin Silicon Oxide Layers. Zack Fleischman<sup>1</sup>, Christian Sandmann<sup>1</sup>, Volkmar Dierolf<sup>1</sup>, Yijie Zhao<sup>1</sup>, Marvin White<sup>1</sup>, M. A. Stolfi<sup>2</sup>, L. Dal Negro<sup>2</sup> and J. Michel<sup>2</sup>; <sup>1</sup>Lehigh University, Bethlehem, Pennsylvania; <sup>2</sup>MIT, Cambridge, Massachusetts.

Following recent reports from Coffa et al.[1] that claim rather high quantum efficiencies, erbium (Er) doped silicon films within MOS structures have gained renewed attention as a possible pathway to obtain silicon based light emitters. Due to the inhomogeneous nature of the oxide films and the lack of lattice sites that are charge neutral, the Er-ion is incorporated in various environments ("sites") leading in regular photoluminescence measurements to a significant line broadening. In films that have been prepared such that they contain silicon nanocrystals, the number of different Er-ion sites is even higher. The large number of sites makes site-specific statements about important quantities, such as emission lifetimes and excitation efficiencies, very difficult. To circumvent this problem, we applied a site-selective excitation scheme in which the ions are excited in two steps using (a) a single laser wavelength capable of exciting two subsequent transitions or (b) two lasers with wavelengths that can be tuned into resonance with the two transitions individually. Applying this scheme under systematic variation of excitation wavelengths (around 1530nm) for the transitions from the 4I15/2 ground state to the 4I19/2 excited state via the 4I13/2 state and detecting the emission (at 980 nm) from 4I11/2 to 4I15/2 leads to a significant line narrowing and a much clearer distinction of the emission features. This gives us the possibility to excite specific sites and study their properties individually. Comparing these results with photoluminescence measured under 488nm excitation, in which the Er-ions are excited through the excitation of the nanocrystals, allows a clear identification of sites that are related to nanocrystals and helps to identify those Er sites that are most effective in electrical excitation. In addition, we studied various excitation schemes in which the ion is excited directly and we found that for excitation around 980nm significant fluorescence line narrowing occurs allowing site-selective studies as well. We will present and discuss applications of these spectroscopic studies for a variety of silicon oxide films that have been grown, doped, and processed under various conditions and demonstrate the value of our technique in our goal to optimize light emission. [1] S Coffa, ME Castagna, M Monaco, A Muscara, and S Loretti, "High efficient light emission devices in silicon," Photonics West, Proc SPIE 2004.

## 11:15 AM <u>V1.6</u>

Optical and Structural Characterizations of ErSiO Crystalline Films Prepared by MOMBE. <u>Hideo Isshiki</u>, Katsuaki Masaki, Kohei Tateishi, Takashi Kawaguchi and Tadamasa Kimura; Univ. of Electro-communications, Tokyo, Japan.

Recently, we reported self-organized formation of ErSiO crystalline superstructures which showed a superlattice structure with a period of 0.9 nm by spin-coating of ErCl3 on Si and two-step annealing process. The ErSiO crystallites showed fine-structured 1.53um PL emissions under the carrier mediated excitation condition at room temperature. It was pointed out that their new ErSiO crystallites contain Er at about 20at% as constituents, not as impurities and therefore have very few non-radiative sites. These ErSiO crystallites are therefore very promising for LEDs, LDs, and optical amplifiers. In order to obtain the ErSiO crystalline films, we have proposed metal organic molecular beam epitaxial growth (MOMBE). In this paper, we show optical and structural characters of the ErSiO crystalline films. MOMBE growths are performed by using TEOS and Er (TMOD)3 as the precursors of Si-O and Er-O respectively. XRD results show crystalline nature but unpublished diffraction pattern for any erbium-silicates in JCPDS file. The single crystalline nature gives fine structures in photoluminescence and its excitation spectra of the Er3+ ions even at room temperature. The PL spectrum at 20K shows a fine structure with the main peak at  $1529\mathrm{nm}$  with a linewidth of 2nm (1meV), which is limited by the monochromator resolution. Because of the crystalline-field caused by a homogeneous medium due to the crystallization, the ground state of 4f-shell in Er ions ( 4I15/2 ) is split into eight clearly. Another unique feature of the ErSiO crystalline compounds is very fast decay of the Er-related emissions. The decay time is about 10 micro second at 20K, which is two to three orders shorter than the decay time usually observed in Er-doped Si. The extreme short decay time is also observed with the crystallization of ErSiO compounds, and is almost temperature independent between 20K and 300K.

## 11:30 AM $\underline{V1.7}$

Photoluminescence Properties of Lamellar Aggregates of Titania Nanosheets Accommodating Rare Earth Ions. Hao Xin, Renzhi Ma, Liangzhou Wang, Yasuo Ebina, Kazunori

Takada and Takayoshi Sasaki; Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Recently, much effort has been made to synthesize luminescence composites by doping rare earth (RE) ions in semiconductor particles such as ZnS, CdS and TiO2 through sol-gel processing or the co-precipitation method, taking advantage of the excellent luminescence characteristics of the RE ions and the stability of the inorganic host. However, Bol et al. reported [1] that RE ions were mostly adsorbed at the particle surface in these doped semiconductors and the characteristic emission of RE ions was not due to the energy absorbed by the host but RE ions themselves. In addition, the doping concentration was limited, generally less than 3%. In this report, a new type of fluorescent semiconductor materials was synthesized by re-stacking the titania nanosheets of Ti0.91O2 having a molecular thickness [2] with Eu3+ or Tb3+ ions (denoted as ex-Ti0.91O2/Eu and ex-Ti0.91O2/Tb, respectively, ex- means exfoliated). The composites were examined by elemental analysis, XRD, TEM, UV-vis absorption and photoluminescence spectroscopy. Characterizations revealed that the composites had a lamellar structure with a gallery height of 1.06 nm and a doping concentration as high as 10 mol% was achieved. The composite of ex-Ti0.91O2/Eu exhibited intense characteristic emission from Eu3+ either by exciting the Ti0.91O2 host with UV light (< 350 nm) or by directly exciting Eu3+ at a longer wavelength where there was no absorption by Ti0.91O2, which suggests that this material has potential applications in optoelectronic devices. In contrast, no energy transfer was observed in the composite with Tb3+. The difference in photoluminescence behavior can be understood by a relative position of excited energy levels of RE ions with respect to the defect states of titania nanosheets. References [1] A. A. Bol, R. V. Beek and A. Meijerink, Chem. Mater. 14, 1121 (2002). [2] T. Sasaki, M. Watanable, H. Hashizume, H. Yamada and H. Nakazawa, J. Am. Chem. Soc. 118, 8329 (1996).

#### 11:45 AM V1.8

Optical Properties of the Er-1 Center in Si/Si:Er Multilayers. Salvatore Minissale<sup>1</sup>, N. Q. Vinh<sup>2</sup>, M. A. J. Klik<sup>1</sup>, Tom Gregorkiewicz<sup>1</sup> and Z. F. Krasil'nik<sup>3</sup>; <sup>1</sup>Van der Waals-Zeeman Institute, University of Amsterdam, Amsterdam, Netherlands; <sup>2</sup>FOM Institute for Plasma Physics Rijnhuizen, FOM, Nieuwegein, Netherlands; <sup>3</sup>Institute for Physics of Microstructures, Institute for Physics of Microstructures, Nizhny Novgorod, Russian Federation.

Research on optical properties of Si continues to be spurred by prospects of integration of electronic and photonic components and by the great possibilities of the highly developed Si technology. Si doped with erbium is studied for light emission, but it features serious disadvantages like quenching of luminescence at high temperature and low concentration of optically active centers. A possible solution to these problems could be offered by Si nanostructures. In the presented study, we carried out a detailed investigation of excitation mechanisms of the  $\mathrm{Er}^{3+}$  in Si nanolayers prepared by SMBE. We have used sandwich structures of interchanged Si/Si:Er nanolayers, with different thickness of both Si and Si:Er layers. A unique optically active Er center, Er-1, was found in these materials in previous investigations. Several lines related to the Er-1 center, with a very small linewidth of  $\Delta E < 10 \mu eV$ , had been resolved [1, 2]. The experiments have been performed under pulsed and cw excitation, in a wide range of flux and wavelengths of the exciting light. All measurements were done at low temperature. PL measurements revealed that emission intensity from a nanolayered structure containing spacers of undoped Si is much stronger than from one thicker layer. This could be explained upon assumption that under illumination excitons are generated in the "spacers" of undoped Si and diffuse into the doped layers to excite Er<sup>3+</sup> ions. This possibility is supported by the fact that PL intensity does not increase above certain thickness of Si:Er layers. The decay characteristics of the PL intensity at  $\lambda$ =1538 nm for a pulsed excitation at a wavelength of 520 nm, obtained for different values of photon flux, feature a fast and a slow component, with the ratio of relevant amplitudes increasing with the flux. This can be interpreted in terms of the Auger process with free carriers that becomes significant at high excitation density. The excitation cross section of Er-1 center was determined upon cw excitation with the 514,5 nm line of an Ar<sup>+</sup> laser to be in the order of  $\sigma$  $\approx$ 6×10<sup>-15</sup> cm<sup>2</sup>. This value is in agreement with the one determined under pulsed excitation. By varying the wavelength, the excitation cross section was found to scale with the absorption cross section of Si. This implies that the Er-1 excitation process remains the same, while only the number of generated e-h pairs changes. The percentage of Er atoms attaining optical activation in nanostructures has been estimated by comparison with a well characterized SiO2:Er material. In that way, we concluded that, depending on peculiarities of the structure, up to 32 % of Er atoms present in the sample form Er-1 centers and contribute to PL. Eventually, formation of Er-1 centers represent a conceivable way to improve low temperature photonic properties of Si:Er. [1] N.Q. Vinh et al., Phys. Rev. Lett. 90, 066401 (2003). [2] N.Q. Vinh et al., Phys. Rev. B 70, 115332 (2004).

SESSION V2: Silicon Nanocrystals Chairs: Yasufumi Fujiwara and Albert Polman Tuesday Afternoon, March 29, 2005 Room 2009 (Moscone West)

## 1:30 PM \*V2.1

Energy Exchange between Silicon Nanocrystals and Er Ions. Minoru Fujii, Department of Electrical & Electronics Engineering, Faculty of Engineering, Kobe University, Kobe, Japan.

Si nanocrystals act as an efficient photosensitizer for Er ions. By doping Si nanocrystals into Er doped silica glasses, effective excitation cross-section of Er ions is strongly enhanced. We have studied in detail the energy transfer mechanism by controlling the size of Si nanocrystals in a wide range, and revealed that there are two energy transfer processes. The first one is a trap-mediated process similar to that observed for Er doped bulk Si crystals, and the other one is direct interaction between excitons and Er ions, which is a characteristic process for nanocrystal systems. The efficient energy transfer means that energy back-transfer is also efficient. Fortunately, enlarged bandgap of Si nanocrystals prevents excitation of electron-hole pairs by energy back transfer from Er ions. This results in very small temperature quenching of luminescence. However, if excess carriers exist in nanocrystals, energy back transfer by giving kinetic energy to the excess carriers becomes possible. In this paper, we will discuss both forward and backward energy transfer processes for SiO<sub>2</sub> films containing Si nanocrystals and Er by controlling the size, kind of dopants, and doping levels of Si nanocrystals in wide ranges.

#### 2:00 PM V2.2

Energy Back Transfer from Er<sup>3+</sup> to Si-nc's in SiO<sub>2</sub>. Ignacio Izeddin, M. A. J. Klik and T. Gregorkiewicz; Van der Waals-Zeeman Institute, University of Amsterdam, 1018XE Amsterdam, Netherlands.

Silicon nanocrystals (Si-nc's) are commonly used to enhance efficiency of Er photoluminescence (PL) in SiO<sub>2</sub> matrices. Energy transfer from Si-nc's to Er is of paramount importance, its related transfer time is estimated to be in the order of microseconds and leads to saturation of Er PL under high flux pulsed pumping regime. With such a slow transfer, during an excitation pulse of several nanoseconds, one nanocrystal will be able to transfer energy to a single Er<sup>3</sup> [1]. Recently, a possibility of a much faster transfer, in the order of nanoseconds, has been suggested. This is investigated in the present report. We have studied a set of SiO<sub>2</sub> samples doped with high concentrations of Er and Si-nc's, for which the fast transfer time was reported [2]. The PL spectra of this material were showing emission from Er3+ ions and Si-nc's, thus being apposite for the study of energy transfer between the two subsystems. The PL experiments have been performed using a tunable Nd:YAG-pumped OPO as excitation source; the detection system (spectrometer and a photomultiplier tube) allowed recording time-resolved PL. We have observed two components in the decay kinetics of Er<sup>3+</sup> PL: a fast initial decay, followed by a slower one. The PL integrated only over the initial fast part shows an identical spectrum to that of a complete signal. Moreover, the fast component has the same decay time as the PL from the Si-nc's, observed simultaneously in the same sample. This suggests a strong coupling between Er<sup>3+</sup> and Si-nc's. Additional evidence of this is found in the similarity of excitation flux dependences for both Er<sup>3+</sup> and Si-nc's PL, where a linear characteristic becomes dominant at higher photon densities. These findings can be rationalized considering energy back transfer from Er<sup>3+</sup> to Si-nc's, leading to additional Si-nc's PL. In this process, energy from an Er<sup>3+</sup> ion -excited previously by an exciton from a Si-nc- flows back to the nanocrystal, relaxing radiatively as excitonic-related luminescence. Such a reversal of the excitation process has not been reported before for the  $\mathrm{SiO}_2$ :Er, Si-nc system. We suggest that its appearance is related to the fast transfer time measured in these samples. This could be understood if we assumed that part of the Er<sup>3+</sup> ions are localized inside the Si-nc's rather than in the SiO<sub>2</sub> matrix. Such a location would provide a better coupling to the Si-nc's, resulting in a faster and more efficient excitation, but also giving rise to the energy back transfer. This hypothesis needs to be corroborated by future studies, however. In a currently prepared experiment, the sample will be excited by a sequence of two high power pulses from Nd:YAG lasers, of which the initial one leads to saturation of Er<sup>3+</sup> PL. Subsequently, by tuning the delay of the second laser pulse, the energy transfer time can be directly measured. [1] M. Wojdak et al., Phys. Rev. B 69, 233315 (2004) [2] M. Fujii et al., J. Appl. Phys. 95, 272 (2004)

## 2:15 PM V2.3

X-ray Analysis of Erbium Doping in Group IV Nanocrystalline Materials. Robert W. Meulenberg, Tony van Buuren, Trevor M. Willey, Jonthan R. I. Lee and Louis J. Terminello; Lawrence Livermore National Laboratory, Livermore, California.

We have produced erbium-doped germanium nanoparticles using a new two cell physical vapor deposition system. Doped nanoparticles are fabricated using two methods: 1) by co-evaporation of Er and Ge and 2) by Er deposition on the surface of undoped Ge nanoparticles. Using elemental specific x-ray techniques [x-ray absorption (XAS) and photoemission (PES) spectroscopy], we are able to monitor band edge shifts as a function of both particle size and Er concentration. In addition, we have used XAS and PES to probe the chemical environment of Er in Ge nanoparticles. We find that large Er/Ge ratios lead to strong spectroscopic signatures in the core level PES spectra. Lower Er/Ge ratios show very little effects in the core level spectra; however, the valence band density of states is altered which allows PES to probe dilute concentrations of Er in Ge nanoparticles. Impact of Er doping on the Ge nanoparticle electronic structure will be discussed. This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, and performed under the auspices of the U. S. DOE by LLNL under contract No. W-7405-ENG-48.

#### 2:30 PM V2.4

Formation and Oxidization of Silicon Nanocrystals in Erbium-Doped Silicon-Rich Silicon Oxide. Xiaodong Pi<sup>1,2</sup>,

Othman H. Y. Zalloum<sup>1,2</sup>, Jacek Wojcik<sup>1,2</sup>, Michael Flynn<sup>1,2</sup>, Andrew P. Knights<sup>1,2</sup>, Peter Mascher<sup>1,2</sup>, Andrew D. W. Todd<sup>3</sup>, William N. Lennard<sup>3</sup> and Simpson J. Peter<sup>3</sup>; <sup>1</sup>Engineering Physics, McMaster University, Hamilton, Ontario, Canada; <sup>2</sup>Centre for Electrophotonic Materials and Devices, Hamilton, Ontario, Canada; <sup>3</sup>Department of Physics and Astronomy, University of Western Ontario, London, Ontario, Canada.

In-situ Er-doped silicon-rich silicon oxide (SRSO) films grown by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) have been annealed in the temperature range from 800 to 950 °C in argon and oxygen atmospheres. Using photoluminescence (PL) measurements at room temperature we find that light emission around 1.53  $\mu m$  is most intense after annealing at  $875~{}^{o} ilde{\mathrm{C}}$  in an argon ambient. This is a result of the compromise between optimum values of Si nanocrystal concentration and size, which have contradictory effects on the distance between Si nanocrystals and Er ions and thus on the PL intensity. The nucleation rate of Si nanocrystals increases with temperature, however, they appear to stabilize at a critical size which increases with annealing temperature. Thus we observe shorter annealing times are required to achieve the maximum PL intensity as annealing temperature increases. The PL intensity saturates after long annealing time at all temperatures. From these measurements we are able to determine the formation energy of the Si nanocrystals, which is controlled by Si diffusion. The effect of annealing in an oxygen ambient has also been observed. The oxidization of Si nanocrystals begins as their nucleation process completes. Thus for long annealing times, the dominant process is the consumption of the Si nanocrystals via thermal oxidization. We observe a decrease in PL intensity and hence a decrease in the efficiency of the energy transfer from nanocrystals to Er ions during the formation of this nanocrystal-surface oxide. Calculation of the activation energy governing this decrease in intensity is consistent with that measured previously for oxygen diffusion in SiO2. Transmission Electron Microscopy (TEM) is being used to characterize the change of the Si nanocrystal size in the oxidation process.

# 2:45 PM $\underline{V2.5}$

Control of Energy Transfer from Si Nanocrystals to Er Ions by Altering Photonic Mode Density. <u>Toshihiro Nakamura</u>, Minoru Fujii and Shinji Hayashi; Department of Electrical and Elecronics Engineering, Faculty of Engineering, Kobe University, Kobe, Hyogo, Japan.

Energy transfer is of fundamental importance in many areas of science. A common mechanism for such transfer is Förster type Coulombic interaction. This process is of increasing importance as a means of improving the efficiency of light emitting diodes. Recently, it has been proposed that the Coulombic interaction can be modified by microcavities and metal structures in which the local photonic mode density (PMD) is altered. Recent experiments on a microcavity containing organic molecules as a donor and an acceptor have demonstrated that the energy transfer rate is influenced by PMD. Similar approach should also be applicable to inorganic systems. In this work, we attempt to control energy transfer from Si nanocrystals (Si-nc) to Er ions by altering PMD. We study time transient of PL from Ér ions in SiO2 films containing Si-nc and Er by systematically changing the distance between the layer and an Au thin film. We observe delayed PL from Er ions, i.e., after pulsed excitation of Si nanocrystals, PL intensity of Er ions continues to rise. The PL delay is the direct evidence for sensitized excitation of Er ions and the

energy transfer time can be estimated from the analysis of the rising part. The energy transfer time showed a strong dependence on the distance between the Er active layer and an Au thin film. The distance dependence can be well explained by the modification of PMD in active layers caused by the presence of an Au thin layer. To our knowledge, this is the first demonstration that the transfer rate from excitons in semiconductors to rare-earth ions can be controlled by PMD.

#### 3:30 PM \*V2.6

Optical Gain in Strongly Coupled Erbium-doped Silicon Nanocrystals Annealed at Low Temperatures. Luca Dal Negro <sup>1</sup>, Michael Stolfi<sup>1</sup>, Jurgen Michel<sup>1</sup>, Xiaoman Duan<sup>1</sup>, John LeBlanc<sup>2</sup>, Jack Haavisto<sup>2</sup> and Lionel Kimerling<sup>1</sup>; <sup>1</sup>Materials Science, MIT, Cambridge, Massachusetts; <sup>2</sup>Charles Stark Draper Laboratory, Cambridge, Massachusetts.

Erbium and silicon nanocrystal (Si-nc) co-doped SiO2 slab waveguides were fabricated on silicon (Si) substrates by reactive radio-frequency (RF) magnetron sputtering followed by a single thermal annealing step. In the presence of Si-nc the Er emission is maximized at annealing temperatures between 600 °C and 700 °C, where the 1.54  $\mu$ m emission is enhanced by more than two orders of magnitude relative to reference Er in SiO2 samples. For samples annealed at 600 °C, pump dependent variable stripe length (VSL) measurements indicate optical gain of 4 cm  $^{-1}$  at 1.54  $\mu$ m. A large coupling coefficient  $\gamma$ c= 150 x 10-15 cm $^3$ /s between Er ions and Si-nc was found by using a simple coupled rate equation model to describe both the optical emission and the gain data. The fitting of the gain versus pump power data requires a Si-nc density which is almost one order of magnitude higher than the one deduced by TEM analysis on the samples annealed at 1100  $^{\circ}$ C According to classical nucleation and growth theory, the lower annealing temperature of 600 °C yields a higher density of smaller Si-nc than the standard 1100 °C annealing. Therefore, the enhanced radiative rate associated with small Si clusters yields a higher coupling factor  $\gamma c$  that, together with a larger Si-nc density, explains the stronger sensitization effect that we have experimentally observed at 600  $^{\circ}\mathrm{C}$  for the first time. The effect of the annealing temperature on the coupling factor  $\gamma c$  will also be highlighted for the first time through power dependent VSL analysis. These Er:Si-nc films can be used to fabricate compact waveguide optical amplifiers and integrated light sources with full CMOS compatibility.

## 4:00 PM <u>V2.7</u>

High-Rate Deposition of Rare-Earth Doped Silicate Nanoparticles for Porous and Dense Optical Films.

<u>Craig Horne</u><sup>1,2</sup>, Pierre de Mascarel<sup>3</sup>, Russell Blume<sup>3</sup>, Jesse Jur<sup>3</sup>,

<u>Cecile Cohen-Jonathan<sup>3</sup>, Michael Chapin<sup>3</sup>, Jonathan Posner<sup>3</sup> and William McGovern<sup>2</sup>; <sup>1</sup>Kainos Energy, San Jose, California; 

<sup>2</sup>NanoGram Corporation, San Jose, California; <sup>3</sup>NeoPhotonics Corporation, San Jose, California.</u>

Laser Reactive Deposition  $(LRD^{TM})$  is a novel process for depositing multicomponent nanoparticles covering a wide range of compositions at high rates for production of porous and dense films. This talk shows results of using  $\mathrm{LRD}^{TM}$  processes for fabricating rare-earth containing glass films. The results are presented in terms of compositional complexity and versatility, microstructures, physical and optical properties, uniformities, and repeatability of multicomponent, rare-earth containing glass films used in the fabrication of erbium-doped planar amplifiers (PLCs). Glass films were synthesized by consolidation of nanoparticulates coated onto silicon substrates with thermal  $SiO_2$  (TOX) layers using LRD<sup>TM</sup> Erbium-doped borophosphosilicate (EBPS), Erbium-doped borophosphoaluminosilicate (EBPAS), and erbium-doped sodium aluminosilicate (ENAS) glass systems have been demonstrated for active core films. Precursors were delivered using an aerosol delivery route due to the low vapor pressure of erbium and sodium compounds. TOX substrates up to 100 mm diameter were used with final film thicknesses ranging from 1 to 8 microns. As-deposited layers were comprised of networked nanoparticles of uniform primary size distribution and average primary size as low as  $12~\mathrm{nm}$ . Thickness uniformities of less than 2% (one std. dev.) and refractive index uniformities less than 0.0005 (one std. dev.) were routinely achieved. Er lifetime and photoluminescence were performed to assess the active properties of the films. Er excited state lifetimes greater than 8 ms and PL spectra with FWHM greater than 40 nm have been attained in films with Er concentrations on the order of 10<sup>20</sup> ions/cc. Optical loss of EBPS films was measured at the telecom C-band, 1550 nm, and found to be 0.1 dB/cm. The low optical attenuation is indicative of low impurity content and low level of defects in glass films densified from  $\mathrm{LRD}^{TM}$ -produced nanoparticle coatings. The high quality of the physical and optical properties along with the cost benefits associated with high speed deposition demonstrate that films produced using  $\mathrm{LRD}^{TM}$  technology are suitable for active planar lightwave circuits for telecom applications.

## 4:15 PM <u>\*V2.8</u>

Pump-probe Experiments in Er-doped Silicon-rich Oxide Slab Waveguides. <u>Manuel Forcales</u>, Nathanael Smith and Robert Elliman; Electronic Materials Engineering, Australian National University, Canberra, Australian Capital Territory, Australia.

Erbium (Er) doped photonic materials and structures continue to attract considerable attention due to possible applications in telecommunications at a wavelength of 1.54 um. Photo-excitation of Er ions in an insulator is generally achieved by resonant high power pumping with a laser. However, efficient non-resonant excitation has been demonstrated in the presence of silicon nanocrystals (Si-nc), when both are present in the same silica substrate. The nanocrystals are believed to act as a sensitizer, absorbing incident radiation over a wide spectral range and coupling it efficiently to Er3+ ions. In comparison with Er-doped bulk silicon, this new medium (SiO2:Si-nc+Er) shows a strong room temperature 1.54 um emission due to a reduction in non-radiative recombinations. This raises the possibility of making a room-temperature optical amplifier that operates under broad band pumping. To this end, we have examined the optical properties of slab waveguides containing Si nanoclusters and Er ions under optical pumping conditions. Optical pump-probe measurements were performed on Er-doped slab waveguides, with excess silicon in the form of nanoclusters or nanocrystals. A  $1.5\ mu\mathrm{m}$ probe beam was prism coupled into the waveguide and its intensity monitored as it exited the edge of the guide. The temporal response of this signal was then measured as the waveguide was optically pumped from above, using either continuous or pulsed excitation. Induced absorption (losses) of the 1.5 mum probe beam in Er-doped and un-doped silicon nanocrystalline waveguides was observed in all cases. However, the magnitude of the induced absorption and the time evolution of its recovery were found to depend on the sample preparation conditions. Importantly, measurements on waveguide structures annealed at temperatures below that required for the formation of silicon nanocrystals were found to exhibit minimal induced absorption. Previous studies have shown that amorphous clusters exhibit sensitizing behavior similar to that of nanocrystals. In this contribution, we present an overview of previous reports of optical gain and compare them with our results. The pump-probe experiments will be discussed in detail and the sensitizing effect of silicon nanoclusters will be explored as a means of minimizing induced absorption in amplifier structures.

> SESSION V3: RE-Doped GaN and Related Materials Chairs: Minoru Fujii and Michal Lipson Wednesday Morning, March 30, 2005 Room 2009 (Moscone West)

## 8:30 AM <u>\*V3.1</u>

GaN:Eu Interrupted Growth Epitaxy: Thin Film Growth and Electroluminescent Devices. Chanaka Munasinghe<sup>1</sup>, A. J. Steckl<sup>1</sup>, E. Nyein<sup>2</sup>, U. Hommerich<sup>2</sup>, H. Peng<sup>3</sup>, H. Everitt<sup>3</sup>, Z. Fleischman<sup>4</sup>, V. Dierolf<sup>4</sup> and J. Zavada<sup>5</sup>; <sup>1</sup> Electrical Engineering, University of Cincinnati, Cincinnati, Ohio; <sup>2</sup> Department of Physics, Hampton University, Hampton, Virginia; <sup>3</sup> Department of Physics, Duke University, Durham, Virginia; <sup>4</sup> Department of Physics, Lehigh University, Bethlehem, Pennsylvania; <sup>5</sup> Army Research Office, Research Triangle Park, North Carolina.

Interrupted Growth Epitaxy (IGE) growth technique was developed as an attempt to optimize GaN:RE electroluminescence (EL) devices. In conventional MBE all molecular beams are incident upon the growth surface simultaneously during the entire growth. A variation of MBE is migration enhanced epitaxy (MEE) wherein each individual beam is incident repeatedly onto the substrate for rather short periods (~seconds). IGE is a combination of conventional MBE and MEE. In IGE, rather long growth periods (~minutes) are used where all beams are incident on the substrate followed by periods where only selected beams are incident. In GaN, it is known that N incorporation rate is much less than that of Ga. IGE is designed to eliminate this problem, with the GaN film being periodically exposed to the N beam only while the growth is interrupted. Hence, the IGE film growth occurs in a periodic fashion, with the shutters of group III elements (Ga and Eu) being open (ON) for a part of the cycle and closed (OFF) throughout the rest of time. The group V is ON during the entire IGE cycling time. The ON times are varied from 5 to 60min. From our initial experiments we determined that material growth occurs only during the ON time. To maintain a constant  $60 \mathrm{min}$ growth time, the IGE cycles were repeated accordingly (i.e. 12 times for 5min IGE, 4 times for 15min IGE, etc.). The 60min growth sample experienced continuous growth, corresponding to conventional MBE growth. The Eu incorporation in the films was approximately the same at  $\sim 0.5$  at.%, which is below the onset of luminescence concentration quenching. Above band gap excitation showed a strong

influence of the ON time on the emission intensities of various Eu transitions. The main emission peaks were at  $\sim$ 621nm and  $\sim$ 632nm. For GaN:Eu films grown on Si substrates, the 20min IGE displayed a 200% enhancement in intensity over the MBE (60min IGE). For films grown on glass substrates, the 15min IGE showed an enhancement of 30% over the MBE. We also observed a change in the highest intensity emission from the 618nm to the 621nm with reduction in ON time. This observation shows the possibility of Eu3+ ions locating at different sites within the GaN lattice at various group III cycling conditions. AC EL devices were fabricated using the IGE-grown GaN:Eu and thick dielectric layers. These devices produced a luminance of  $\sim 1000 \text{ cd/m} 2$  at an efficiency of  $\sim 0.15 \text{ lm/W}$ . This luminance is  $12 \times$  that reached through MBE growth. The optimized IGE GaN:Eu device has nearly-ideal phosphor characteristics with reduced below-threshold leakage and sharp above-threshold L-V slope. Our overall goals in IGE are to understand in detail the Eu3+ incorporation and optical activation mechanisms and to optimize GaN:RE EL devices. In addition to the growth and device results presented in this paper, companion papers will present detailed investigations of the optical properties of GaN:Eu IGE films using a variety of characterization techniques.

#### 9:00 AM V3.2

Luminescence and Lifetime Properties of Europium Doped Gallium Nitride Compatible with CMOS Technology. Carl Poitras, Michal Lipson, Huaqiang Wu and Michael G. Spencer; Electrical and Computer Engineering, Cornell University, Ithaca, New York

The doping of wide band gap materials like GaN with rare earth (RE) elements such as erbium and europium allows for reduced quenching of the emission of the RE ions, resulting in their increased room temperature emission. LEDs using GaN:Eu have already been demonstrated. The many colors available from RE ions make them appealing from full color displays telecommunication applications. Here we study europium doped gallium nitride which is in powder form. This powder can easily be spun into thin films on substrates like silicon wafers. The films can withstand high temperatures, up to approximately 1000 C, opening the door to active structures compatible with CMOS technology. The powder is obtained by heating a gallium/europium mix in an argon ambient to 1000 C, at which point an ammonia ambient is used. The furnace is then kept at the same temperature for a few hours. Bismuth is also used as a wetting agent. We measured the luminescence of the powder using a  $16~\mathrm{mW}$  HeCd laser. The powder exhibits a strong luminescence at 621nm when pumped with the laser above gap at 325 nm, indicating an efficient energy transfer from the crystal to the rare earth ions. The relatively long lifetime of the Eu opens the door to on-chip active devices based on population inversion including amplifiers and light emitters. In order to analyze the energy transfer process in these films, we present a study of the emission and lifetime dependence of the films as a function of pump power, wavelength and temperature.

## 9:15 AM <u>V3.3</u>

Infrared Emission from Er-doped III-N Light Emitting Diodes. John Zavada, <sup>1</sup>Electronics, Army Research Office, Durham, North Carolina; <sup>2</sup>Physics, Hampton University, Hampton, Virginia; <sup>3</sup>Physics, Kansas State University, Manhattan, Kansas; <sup>4</sup>SVTA, Eden Prairie, Minnesota.

We report on the infrared emission of Er-doped III-N light-emitting diodes (LEDs). The quantum well-like device structures were grown through a combination of metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) on c-plane sapphire substrates. The AlGaN barrier layers, with an Al concentration of  $\sim$ 12%, were prepared by MOCVD and doped with Si or Mg to achieve the n-type and p-type conductivity, respectively. The thickness of Er-doped GaN quantum well-like regions, grown by MBE, ranged from 5 nm to 200 nm. The Er concentration was estimated to be ~  $1018\text{-}1019~\mathrm{cm}\text{-}3.$  The dual stage growth process was used to take advantage of the high quality of AlGaN layers produced by MOCVD and in situ doping of Er during MBE growth. Subsequently, the multilayer structures were processed into LED devices using a standard process. A variety of LEDs with different sizes and geometric shapes were produced. The processed LED structures were first examined using above bandgap and below bandgap optical excitation. Infrared photoluminescence (PL) spectra displayed narrow infrared emission lines, at 1.0 and 1.5 microns, representative of the Er3+ system. Under either forward or reverse bias, electroluminescence (EL) from the LEDs was observed at the same emission lines. While the EL spectra under reverse bias were similar to the PL data, forward biasing of the LEDs produced a weaker, broader infrared emission. The L-I and I-V characteristics of these devices were measured at and above room temperature. From the L-I characteristics the product of effective excitation cross-section and lifetime of GaN:Er LEDs was determined. Estimates of the excitation cross-section were obtained and compared to results made in the visible.

## 9:30 AM $\underline{V3.4}$

Optical Spectroscopic Studies of Eu3+ Centers in GaN. Hongying Peng<sup>1</sup>, Chong-Won Lee<sup>1</sup>, Henry O. Everitt<sup>2.1</sup>, John M. Zavada<sup>2</sup>, Dong-Seon Lee<sup>3</sup>, Chanaka Munasinghe<sup>3</sup> and Andrew J. Steckl<sup>3</sup>; <sup>1</sup>Physics, Duke University, Durham, North Carolina; <sup>2</sup>US Army Research Office, Research Triangle Park, North Carolina; <sup>3</sup>Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio.

In recent years doping of GaN by various rare earth (RE) ions has become of considerable scientific and technological interest. Optimization of GaN:Eu-based luminescent devices requires a more detailed understanding of the incorporation, excitation, and emission properties of Eu3+ ions in the GaN host matrix. In the present study, time-resolved photoluminescence (PL) and photoluminescence excitation (PLE) measurements were employed to study the relaxation dynamics of the red luminescence (5D0→7F2) from GaN:Eu as a function of pump energy. For optical excitation at the GaN exciton energy, the red emission exhibits the strongest intensity, and the decay transients are almost unchanged at 77K and 300K, indicating a remarkably efficient energy transfer process independent of temperature. However, for excitation energies above the GaN band edge or into the PLE absorption tail below the band edge, the red luminescence shows clear excitation wavelength- and temperature-dependent behavior. An energy transfer mechanism based on the data will be discussed. Moreover, the continuous-wave PL measurements clearly indicate two classes of 4f-4f transitions of Eu3+ ions in GaN - those that luminesce for photoexcitation just below the GaN band gap and those that do not. PLE measurements indicate a broad absorption tail extending 550 meV below the GaN band gap for the former transitions (category I) while indicating no below-gap absorption tail for the latter transitions (category II). Multi-component PL fine structure is observed for many transitions, especially the 5D0 \rightarrow 7F0, 7F1, 7F2 and 7F3 transitions. Based on the PLE measurements and the fine structure observed for the  $5D0 \rightarrow 7F0$ transition, at least two and perhaps as many as five Eu3+ centers can be claimed. Using wavelength-tunable femtosecond pulsed laser excitation and a streak camera operated in photon-counting mode, a total of 37 emission lines and transition decays from the 5D2, 5D1 and 5D0 upper levels to the 7FJ (J = 0, 1, 2, 3) lower levels have been measured within the visible spectral region 1.7-2.8 eV. Using spectral clustering and emission decay constants, assignment of these emission lines has been attempted. Single exponential fitting of the emission decay shows that the 5D1 \rightarrow 7FJ and 5D2 \rightarrow 7FJ transitions for both Eu3+ centers have a decay constant of 2.8  $\mu s$  and 2.4  $\mu s$ , respectively. These decays are much faster than the bi-exponential decay of the 5D0 $\rightarrow$ 7FJ transitions whose typical decay constants are  $\sim$ 30  $\mu s$  and  $\sim$ 180  $\mu$ s. Moreover, pump absorption, energy transfer, the radiative and non-radiative relaxation mechanisms of Eu3+ ions were found to depend slightly on their local crystal environment. Emission from category I  $\mathrm{Eu}3+$  centers generally decays more slowly than from category II centers for the same transition.

## 9:45 AM <u>V3.5</u>

Excitation-Wavelength Dependent and Time-Resolved Photo-Luminescence Studies of Europium Doped GaN Grown by Interrupted Growth Epitaxy (IGE). EiEi Nyein<sup>1</sup>, Uwe Hommerich<sup>1</sup>, Chanaka Munasinghe<sup>2</sup>, Andrew J. Steckl<sup>2</sup> and John M. Zavada<sup>3</sup>; <sup>1</sup>Department of Physics, Hampton University, Hampton, Virginia; <sup>2</sup>Dept. of Electrical and Computer Eng., University of Cincinnati, Cincinnati, Cincinnati, Ohio; <sup>3</sup>Army Research Office, Research Triangle Park, North Carolina.

We report on the photoluminescence properties of Eu doped GaN samples prepared by interrupted growth epitaxy (IGE). IGE was recently developed at the University of Cincinnati in an effort to optimize the red emission properties of GaN: Eu for display applications. During IGE the group III shutter is closed for a certain time interval, which allows the GaN: Eu film to compensate for any nitrogen deficiency. Improvements in the GaN: Eu electroluminescence device performance by more then an order of magnitude were observed from GaN: Eu films grown by IGE compared to conventional MBE. In this work, we present results of excitation-wavelength dependent and time-resolved photoluminescence (PL) studies of GaN: Eu samples grown by interrupted growth epitaxy. The Ga-shutter cycling time was varied from 5-30 minutes. 5 minutes were added to the corresponding group V cycling times to allow nitridation of the film. Each cycle was repeated to yield a total growth time of 60 minutes. Under above-gap excitation (333-363nm), large differences were observed in the Eu3+ PL intensity and spectral features as a function of Ga cycling time. The overall strongest red Eu3+ PL intensity was obtained from a sample grown with a Ga cycling time of 20 minutes. The main Eu3+ emission line originating from the 5D0->7F2 transition was composed of two peaks at 620 nm and 622 nm, which varied in relative intensity depending on the growth conditions. The room-temperature emission lifetimes of the samples were non-exponential and varied from  $\sim 50~\mu s$ 

to  ${\sim}200\mu s$  (1/e lifetimes). Interestingly, the shortest emission lifetime under above-gap excitation was observed from the GaN: Eu sample exhibiting the strongest red Eu3+ PL intensity. Significantly different Eu3+ PL properties were observed from this set of GaN: Eu samples under resonant excitation at 471 nm (7F0->5D2). Independent of Ga cycling time, all samples exhibited nearly identical PL spectra under intra-4f Eu3+ excitation with a dominant PL line located at 622 nm. Moreover, the Eu3+ PL intensities and lifetimes varied significantly less compared to above-gap excitation. The excitation wavelengths dependent PL results indicate the existence of different Eu3+ centers in GaN: Eu, which can be controlled by the Ga shutter cycling time. More results of temperature and excitation wavelength dependent PL studies will be presented at the conference.

#### 10:30 AM \*V3.6

Combined Excitation Emission Spectroscopy of Rare Earth Ions in GaN and AlGaN Films. Volkmar Dierolf, Physics, Lehigh University, Bethlehem, Pennsylvania.

Combined excitation emission spectroscopy (CEES) is a powerful tool to investigate and identify different rare ion incorporation sites and their role in various excitation processes. In this technique, a large number (approx. 1000) of emission spectra are recorded for continuously varying excitation wavelengths. The resulting dataset of emission intensities as a function of excitation and emission wavelength gives a comprehensive overview of the spectral feature that allows to produce a fingerprint of the energy levels of the various sites. We will review and compare, recent results obtained with this technique for rare earth doped (i.e.: Er, Eu) GaN and AlGaN active layers that have been prepared by different groups using various methods of growth and rare earth doping. Comparing the luminescence spectral obtained under direct resonant excitation with that obtained under electrical excitation and optical excitation above the bandgap enables us to spectrally identify the incorporation sites that are most effective for optoelectronic devices and find the preparation conditions under which these sites are most abundant.

## 11:00 AM <u>V3.7</u>

Nonequilibrium Carrier Dynamics Studied in Er,O-Codoped GaAs by Pump-Probe Reflection Technique.

Yasufumi Fujiwara<sup>1</sup>, Kazuhiko Nakamura<sup>1</sup>, Shoichi Takemoto<sup>1</sup>, Atsushi Koizumi<sup>2</sup>, Masato Suzuki<sup>3</sup>, Yoshikazu Takeda<sup>2</sup> and Masayoshi Tonouchi<sup>3</sup>; <sup>1</sup>Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Osaka, Japan; <sup>2</sup>Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan; <sup>3</sup>Institute of Laser Engineering, Osaka University, Osaka, Japan.

In GaAs codoped with Er and O (GaAs:Er,O), it has been found that the codoping produces a single atom configuration (Er-2O configuration) as an Er atom located at the Ga sublattice with two adjacent O atoms together with two As atoms, resulting in extremely strong Er Iuminescence. Recently we have fabricated GaInP/GaAs:Er,O/GaInP double heterostructure light-emitting diodes and successfully observed  $1.5\mu\mathrm{m}$  electroluminescence due to an Er-2O center under forward bias at room temperature. However, Er excitation cross section by current injection decreased with increasing active layer thickness, implying reduced diffusion length of injected carriers in a GaAs:Er,O active layer. In this contribution, carrier dynamics in GaAs:Er,O have been systematically investigated by means of a pump and probe reflection technique with a mode-locked Ti:sapphire laser. Time-resolved differential reflectivity of GaAs:Er,O exhibited an abrupt increase in amplitude, followed by a steep decrease to negative in less than 1 ps and then a gradual increase in approximately 100 ps. The steep decrease indicated short lifetime of photoexcited carriers, which was quite coincident with the reduction in diffusion length of injected carriers. The amplitude of the negative differential reflectivity depended strongly on wavelength and power of pump light, and Er and O concentrations, suggesting that a trap induced by Er and O codoping would play an important role in dynamics of nonequilibrium carriers in GaAs:Er,O.

## 11:15 AM <u>V3.8</u>

On 2.7  $\mu m$  Emission from Er-doped Large Band Gap Hosts. Henk Vrielinck <sup>1,2</sup>, Ignacio Izeddin <sup>1</sup> and Tom Gregorkiewicz <sup>1</sup>; <sup>1</sup>Van der Waals-Zeeman Institute, University of Amsterdam, Amsterdam, Netherlands; <sup>2</sup>Department of Solid State Sciences, University of Gent, Gent, Belgium.

Optical emission at the wavelength of 2.7  $\mu m$  is desirable in view of its applications in spatial communications as well as in medical science. In principle, rare earth Er is a good candidate to obtain such emission from an intra-4f shell transition from its second to its first excited state ( $^4I_{11/2} \rightarrow ^4I_{13/2}$ ). In order to investigate this, we have performed photoluminescence experiments on a large band gap semiconductor (GaN) and an insulator (Cs<sub>2</sub>NaYF<sub>6</sub>) doped with Er at different concentrations. The samples were optically excited by a

tunable pulsed Nd:YAG based optical parametric oscillator (OPO) or a Nd:YVO4 based cw laser and time-resolved photoluminescence from the samples, placed in a He flow cryostat at temperatures ranging from 4.2 K up to room temperature, was recorded with a detection system consisting of a spectrometer and a photomultiplier tube. Radiative transitions between different multiplets of the  $\rm Er^{3+}$  ion have been mapped and time-resolved relaxations followed. As a result of the study, a complete diagram of excitation and de-excitation paths has been plotted and characteristics of radiative and non-radiative transitions have been obtained for both systems. Energy relaxations in the 4f shell involving radiative transitions as well as possible energy transfer among  $\rm Er^{3+}$  ions have been cleared up, pointing out the conditions to successfully reach the 2.7  $\mu m$  emission from Er.

#### 11:30 AM <u>V3.9</u>

Energy-Back-Transfer Process in Rare-Earth Doped AlGaN. Akihiro Wakahara<sup>1</sup>, Tetsuya Fujiwara<sup>1</sup>, Hiroshi Okada<sup>1</sup>, Akira Yoshida<sup>1</sup>, Takeshi Ohshima<sup>2</sup> and Hisayoshi Itoh<sup>2</sup>; <sup>1</sup>Electrical & Electronic Eng., Toyohashi Univ. of Technology, Toyohashi, Japan; <sup>2</sup>JAERI, Takasaki, Takasaki, Japan.

We have been investigating the effect of  $Al_xGa_{1-x}N$  on the rare-earth (RE) doping and RE-related luminescence properties, and found that, in case of Eu, Tb, and Er, the luminescence intensity caused by inner-shell transitions of REs was increased with increasing the AlN molar fraction and the line width became broad at the AlN molar fraction around 0.5. These results indicate that local structure, such as ordering or disordering of group-III elements, affect the electronic structure of RE ions. However, effect of AlGaN on the energy-transfer and/or back-transfer processes has not deeply understood. In this study, we investigated time-resolved photoluminescence properties to clarify the energy-back-transfer process in AlGaN with various AlN molar fractions. Eu, Tb, and Er were introduced into Al<sub>x</sub>Ga<sub>1-x</sub>N  $(0 \le x \le 1)$  epi-layers using ion implantation method. A  $1.5\mu$ m-thick  $\overline{Al_x}\overline{Ga_{1-x}}N$  layer was grown on a GaN/sapphire (0001) epitaxial template by organometallic vapor phase epitaxy. The ion implantation was carried out at room temperature with the acceleration energy of 200keV. The dose of RE ions was in the range of 1-10x10<sup>14</sup>cm<sup>-</sup> project range and peak concentration estimated by using TRIM were100nm and 3-30x10<sup>19</sup>cm<sup>-3</sup>, respectively. Implantation damage was recovered by using rapid thermal annealing (RTA) in  $N_2$  at  $1400^{\circ}\mathrm{C}$  for 60s. The time resolved photoluminescence was perfumed by using ArF excimer laser as the excitation source. PL intensity from REs increased super linear as increasing the AlN molar fraction at first, then tend to saturate. Temperature dependence of PL properties reviled that the thermal quenching became small as increasing the Al contents, and also became small as the major emission lines of RE became longer, i.e., from Er (408nm) to Eu (620nm). The decay time of REs used in the present work became shorter as increasing the temperature. From these results, the improvement of PL properties could be explained by using multi-phonon assisted energy-back-transfer model, in which the barrier height for energy-back-transfer process is increased as increasing the Al contents.

## 11:45 AM <u>V3.10</u>

High Resolution Site-Selective Studies of Erbium-Centers in GaN and GaN:Mg. Adrian Kozanecki<sup>1</sup>, Vasyl Glukhanyuk<sup>1</sup>, Hanka Przybylinska<sup>1</sup> and Wolfgang Jantsch<sup>2</sup>; <sup>1</sup>Solid State Spectroscopy, Institute of Physics, Warsaw, Poland; <sup>2</sup>Institute of Semiconductor and Solid State Physics, J. Kepler University, Linz, Austria.

The recent demonstration of visible electroluminescence from rare earth doped GaN has stimulated significant interest in this material for possible applications in color displays. Er-doped GaN is particularly interesting, because of its ability to emit light simultaneously in the infrared and green range of wavelengths. Photoluminescence (PL) spectra of Er near 1 500 nm are complex and depend on many factors, such as Er concentration, growth conditions, annealing temperature as well as co-doping. As a result little is known about the microscopic structure of the optically active Er centers. The wide (3.5 eV) forbidden gap of GaN allows to perform site selective excitation studies aimed to resolve the structure of Stark split electronic levels and, hence, the site symmetry of different centers. In this work we use high resolution resonant optical spectroscopy including Fourier Transform Infrared spectroscopy with the aim to determine the site symmetry of Er3+ ions in GaN and GaN:Mg. Low Er implant doses were used to reduce the number of different centers and to observe sharp well defined PL lines. PL excitation spectroscopy at an energy range corresponding to the 4I9/2 and 4I11/2 absorption is applied to study splittings of the Er3+ energy levels. Site selective excitation of separate centres needs temperatures below 20 K, as energy migration between different Er centres has been observed. For temperatures above 50 K the PL spectra do not seem to depend on particular excitation wavelength, which indicates that energy migration is fast enough to ensure uniform excitation of different Er-centres. The Stark split energy levels serve as a basis for model calculations. Numerical analysis based on point charge model is used

to calculate parameters of local crystal field. The splitting of the excited 419/2 and 4111/2 free Er ion level in weak crystal field of the host material were calculated and good agreement with experimental results was obtained. From the values of crystal field parameters we conclude that Er occupies a substitutional lattice site in the crystal. The symmetry of Er centers is C3v in hexagonal GaN. It is shown that doping with Mg disturbs local symmetry of the centres and results in new PL transitions seen in FTIR measurements. Calculations of the crystals field parameters of an Er centre in GaN:Mg,Er are performed and compared with data obtained for isolated Er-centres.

SESSION V4/FF4: Joint Session: Lasing Materials and Luminescent Devices Chairs: Astrid Aksnes Dyrseth and Tony Peaker Wednesday Afternoon, March 30, 2005 Room 3020 (Moscone West)

#### 1:30 PM \*V4.1/FF4.1

Rare Earth Ion Implantation for Silicon Based Light Emission: From Infrared to Ultraviolet. Wolfgang Skorupa<sup>1,2</sup>, Jiaming Sun<sup>1</sup>, Thomas Dekorsy<sup>1</sup>, Manfred Helm<sup>1</sup>, Lars Rebohle<sup>2</sup>, Thoralf Gebel<sup>2</sup>, Alexei N. Nazarov<sup>3</sup>, Igor P. Tjagulski<sup>3</sup>, Igor N. Osiyuk<sup>3</sup>, Slawomir Prucnal<sup>4</sup> and Jerzy Zuk<sup>4</sup>; Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., Dresden, Germany; Nanoparc GmbH, Dresden, Germany; Institute of Semiconductor Physics, Academy of Sciences of Ukraine, Kiev, Ukraine; Institute of Physics, Maria Curie-Sklodowska-Univ., Lublin,

Using ion implantation different rare earth luminescent centers (Gd3+, Tb3+, Eu3+, Ce3+, Tm3+, Er3+) were embedded into the silicon dioxide layer of a purpose-designed MOS capacitor with advanced electrical performance. The silicon dioxide layer was produced without silicon nanoclusters. Efficient electroluminescence was obtained from UV to infrared with a transparent top electrode made of indium-tin oxide. Electroluminescence properties were analysed regarding luminescence spectra, decay time, impact excitation cross relaxation, and power efficiency. Top values of the efficiency of 0.2 % corresponding to external quantum efficiencies well above the percent range were reached. The electrical properties of these devices such as carrier injection, charge-to-breakdown, charge trapping characteristics, and operation lifetime for dedicated applications were also evaluated. Although former works showed that for a reliable operation of such devices silicon nanoclusters are needed in the silicon dioxide matrix it will be shown that with the advanced MOS capacitors an increase of the operation lifetimes by a factor of 100-1000 is possible. This allows an analysis of the electro-optical and electrical properties at higher current densities without any degradation problem. The recently demonstrated worldwide first ultraviolet silicon-based light emitter [1] was produced with the here presented device type and will be discussed in more detail. Finally application prospects in the field of biosensing will be shown. [1] J.M. Sun, W. Skorupa, T. Dekorsy, M. Helm, L. Rebohle, T. Gebel, Appl. Phys. Lett. 85, 3387 (2004)

## 2:00 PM V4.2/FF4.2

Characterization of Er/O-Doped Si-LEDs with Low Thermal Quenching. Amir Karim, Goran Hansson, Wei-Xin Ni and Anders Elfving; Department of Physics and Measurement Technology, Linkoping University, Linkoping, Sweden.

Electroluminescence studies of MBE-grown Er/O-doped Si-diodes at reverse dias have been done. For some devices there is very reduced thermal quenching of the emission at 1.54  $\mu$ m, there are examples where the temperature dependence is abnormal in that the intensity for a constant current even increases with temperature up to e.g. 80 C. These devices have been studied with cross-sectional transmission electron microscopy to see the microstructure of the Er/O-doped layers as well as the B-doped SiGe-layers that are used as electron emitters during reverse-bias. Although there are defects in the layers there is no evidence for precipitates of SiO2. While reduced thermal quenching often is attributed to having the Er-ions within SiO2 layers or precipitates, this is not the case for our structures as evidenced by our TEM studies. The origin of the abnormal temperature dependence is attributed to the two mechanisms of breakdown in the reverse-biased diodes. At low temperature the breakdown current is mainly due to ionization resulting in low-energy electrons and holes that quenches the intensity by Auger de-excitation of the Er-ions. At higher temperatures the breakdown current is mainly phonon-assisted tunnelling which results in a more efficient pumping with less de-excitation of the Er-ions. Finally at the highest temperatures the thermal quenching sets in corresponding to activation energy of 125 meV, which is slightly lower and thus more favourable than 150 meV that has been reported in other studies.

### 2:15 PM V4.3/FF4.3

High Efficiency Visible Electroluminescence from Silicon Nanocrystals Embedded in Silicon Nitride. Gun Yong Sung<sup>1</sup>, Nae-Man Park<sup>1</sup>, Tae-Youb Kim<sup>1</sup>, Kyung-Hyun Kim<sup>1</sup>, Jaeheon Shin<sup>1</sup>, Kwan Sik Cho<sup>2,1</sup> and Jung H. Shin<sup>2</sup>; <sup>1</sup>Future Technology Research Division, ETRI, Daejeon, South Korea; <sup>2</sup>Dept. of Physics, KAIST, Daejeon, South Korea.

Semiconductor electronics is strongly dominated by silicon technology. However silicon technology does not allow easy integration with optical component since silicon is a poor light emitter. There has been much effort to solve the inability of silicon to act as a light emitting source such as porous silicon, erbium doped silicon, and silicon nanocrystals(nc-Si). Among these, nc-Si dispersed in SiO2 matrix has attracted a great interest because their band gap is enlarged in comparison with bulk silicon due to quantum confinement effects. However, it is reported that due to silicon-oxygen double bonds, nc-Si in SiO2 matrix have localized levels in the band gap and emit light only in the near-infrared range of 700~900nm even when the size of nc-Si was controlled to below 2nm. Previously, we reported that red to blue PL were observed from nc-Si quantum dots as well as amorphous Si quantum dots in silicon nitride matrix.[1,2] Therefore nc-Si in silicon nitride matrix supplies the possibility of Si-based full-color emission. We have fabricated light-emitting diodes (LEDs) with a transparent doping layer on silicon nanocrystals (nc-Si) embedded in silicon nitride matrix formed by plasma-enhanced chemical vapor deposition. Under forward biased condition, orange electroluminescence (EL) with its peak wavelength at about 600nm was observed at room-temperature. The peak position of the EL is very similar to that of the photoluminescence (PL) and the emitted EL intensity is proportional to the current density passing through the device. We suggest that the observed EL is originated from electron-hole pair recombination in nc-Si. By using ITO and n-type wide bandgap semiconducting layer combination as a transparent doping layer, we obtained high external quantum efficiency greater than 2.0%, which is the highest value ever reported in nc-Si based LED. [1] Nae-Man Park et al., Phys. Rev. Lett. 86, 1355 (2001). [2] Tae-Youb Kim et al., Appl. Phys. Lett. Nov. 8, 2004, in press.

## 2:30 PM V4.4/FF4.4

Study of Optical Gain in Thick GaN Epilayers by Variable Stripe Length Technique. Gintautas Tamulaitis<sup>1</sup>, Juras Mickevicius<sup>2</sup>, Michael Shur<sup>2</sup>, Qhalid Fareed<sup>3</sup> and Remis Gaska<sup>3</sup>; <sup>1</sup>Semiconductor Physics, Vilnius University, Vilnius, Lithuania; <sup>2</sup>Department of ECE and CIE, Rensselaer Polytechnic Institute, Troy, New York; <sup>3</sup>Sensor Electronic Technology, Inc, Columbia, South Carolina.

We report on the gain study in high-quality thick GaN layers grown by Metal Organic Chemical Vapor Deposition (MOCVD) at different conditions using the Variable Stripe Length (VSL) technique. The amplification of light propagating along the layer surface (perpendicular to the c-axis of the crystal) and perpendicular to the layer (along the c-axis) for the layers with thicknesses ranging from 1 to 11 ?m was investigated. Peak gain coefficients of up to 7300 cm-1 in the GaN were estimated by fitting the experimental stripe length dependence of the edge luminescence with one-dimensional description of light amplification in medium with positive gain. Involvement of new gain modes after saturation of the highest-gain modes was observed. GaN samples with different optical gains were also characterized using spontaneous photoluminescence spectroscopy, time-resolved photoluminescence technique, and light-induced transient grating technique that allowed us to determine the nonequilibrium carrier lifetimes. Finally, we discuss the limitations of the VSL technique related to the assumption of one-dimensional light propagation, to the high gain saturation due to the light amplification caused by stimulated transitions at the stripe lengths of several micrometers and consider the influence of heating of the photoexcited electron-hole plasma on the light amplification.

## 2:45 PM V4.5/FF4.5

Syntheses and Electro-Optical Properties of Twisted Pi-System Chromophores. Hu Kang, Antonio Facchetti, Hua Jiang, Peiwang Zhu and Tobin J. Marks; Chemistry Department and Materials Research Center, Northwestern University, Evanston,

A series of nontraditional twisted intramolecular charge-transfer (TICT) chromophores were designed and synthesized. These chromophores exhibit ultra-high hyperpolarizabilities (beta) and optical absorption features strongly dependent on the interplanar dihedral angle. The tunable structural characteristic that promotes these optical/nonlinear optical features/responses is a sterochemically enforced reduction of the D-A Pi-conjugation that enforces zwitterionic behavior in the ground state and provides a low-energy and large-oscillator strength intramolecular excitation feature. The

consequence is that molecules with a relatively small number of Pi-electrons exhibit responses far larger than those of corresponding traditional planar Pi-conjugated chromophores. Evaluations of electro-optic devices based on these chromophores are in progress.

SESSION V5/FF5: Joint In-Room Poster Session: Lasing Materials and Luminescent Devices Chairs: Astrid Aksnes Dyrseth and Tony Peaker Wednesday Afternoon, March 30, 2005 3:30 PM - 5:00 PM Room 3020 (Moscone West)

#### V5.1/FF5.1

Influence of Rapid Thermal Annealing on Self-Assembled Quantum-Dot Superluminescent Diodes. Ziyang Zhang<sup>1</sup>, Ying

Yin Tsui<sup>1</sup>, Robert Fedosejevs<sup>1</sup> and Zhanguo Wang<sup>2</sup>; <sup>1</sup>University of Alberta, Department of Electrical & Computer Engineering, Edmonton, Alberta, Canada; <sup>2</sup>Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China.

Superluminescent diodes (SLD) have great potential for application as light sources including optical gyroscopes and sensors, optical time domain reflectometers (OTDR) and wavelength-division multiplexing (WDM) system testing. High output power and large spectral bandwidth are key features for SLD. In recent years, self-assembled quantum dots (SAQD) instead of quantum well have attracted significant attention for laser diodes (LD) application. QD-LD are expected to attain high power, less temperature-sensitive operation, and a remarkable reduction in threshold current, due to the discrete atom-like states in QD. Much of the interest in QD-LD focuses on the uniform growth of QD's to obtain sufficient gain to lase. However, it is noted that non-uniform characteristics of QD size can be beneficial to SLD to realize the desired wide spectral bandwidth. In this work, two kinds of SAQD-SLDs have been fabricated. Both of them were with tilted-stripe active region. The only difference between them was one has been treated with rapid thermal annealing (RTA) while the other has not. Continuous wave (CW) output power of 200mW and a spectral width of 60nm were realized at room temperature by the sample which has not been treated with RTA. In addition, the CW output power of 200mW was obtained at only 1.4A injection current. As a SLD, it was a very high efficiency. However the CW Maximal output power was only 140mW and the spectral width was 40nm of the sample which has been treated with RTA. As we know, the homogeneity of quantum dots can be effectively improved after RTA, and it will generally be beneficial for QD-LD. However, in this case, for QD-SLD, the RTA effect was quite different from that of QD-LD. It indicated that the appropriate inhomogeneity of QD is an important factor to realize high performance Superluminescent diodes. One of the authors (Ziyang Zhang) would like to acknowledge finacial support from the Alberta Ingentuiy Fund.

## V5.2/FF5.2

A Novel Class of Imidazole-Containing Excited-State Intramolecular Proton Transfer Materials: Synthesis and Amplified Spontaneous Emission from a Single Crystal. Sanghyuk Park<sup>1</sup>, Sehoon Kim<sup>1</sup>, Oh-hoon Kwon<sup>2</sup>, Du-Jeon Jang<sup>2</sup>, Sangwoo Park<sup>3</sup>, Moon-Gun Choi<sup>3</sup> and Soo Young Park<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Seoul National University, Seoul, South Korea; <sup>2</sup>School of Chemistry, Seoul National University, Seoul, South Korea; <sup>3</sup>Department of Chemistry, Graduate School, Yonsei University, Seoul, South Korea.

The excited-state intramolecular proton transfer (ESIPT) reactions have been intensively investigated because of the fundamental importance of this process and its potential for practical applications in laser dyes, solar energy concentrators, chemosensors, and electroluminescent materials. To realize a compact and rugged device with better performance, most of the ESIPT applications demand a highly concentrated solid state system. However, it normally happens that the intermolecular interactions in the condensed system raise the problem of significant concentration quenching in the fluorescence intensity, which is an important challenge in the fluorescent ESIPT materials as well. Very recently, we reported highly concentrated but still ESIPT-active solid materials by introducing dendrimer structures, and we have been successful in demonstrating that the fluorescence emission can be greatly enhanced in the aggregated system when the molecular structure is properly designed. As a continued effort in these works, we have designed and synthesized a novel class of ESIPT materials, hydroxy-substituted tetraphenyl imidazole (HPI) and its derivative HPI-Ac, which assumes aggregation-induced enhanced emission (AIEE) in the solid state. Prepared materials showed transparent and well-formed single crystals with intense blue photoluminescence and amplified spontaneous emission (ASE). The structural characteristics of HPI and HPI-Ac

were fully identified by X-ray crystallography. The crystal structures were triclinic and the two phenyl rings at 1- and 5-positions of central imidazole ring are twisted almost perpendicular to the chromophore plane. These two twisted phenyl rings appropriately prevent direct stacking of the active chromophores in a zig-zag manner and maintain proper intermolecular distance, and reduce the concentration quenching of ESIPT fluorescence. The ESIPT kinetics and proton-transfer ASE were studied by an actively/passively mode-locked Nd:YAG laser (Quantel, YG701) and a 10-ps streak camera (Hamamatsu, C2830) attached to a CCD detector (Princeton Instruments, RTE128H). The intrinsic four-level nature of ESIPT contributes to easy population inversion, and the low-threshold ASE from HPI-Ac will be discussed in this work.

#### V5.3/FF5.3

Organic/Inorganic Hybrid Glasses Doped with (Erbium-ions/CdSe nanoparticles) for Laser Amplifiers.

Kyung M. Choi, <sup>1</sup>Bell Labs, Lucent Technologies, Murray Hill, New Jersey; <sup>2</sup>Department of Materials Science and Engineering, University of Illinios at Urbana-Champaign, Urbana, Illinois.

A new family of organic/inorganic hybrid silicate materials, bridged polysilsesquioxanes, was designed and synthesized through a molecular-level mixing technique. By modifying the Si-O-Si polymeric network, we produced controllable, porous glass materials for facile and uniform doping of various ions, metals or semiconductor particles. By taking advantage of void volume created in those molecularly modified silicate systems, we developed hexylene- or fluoroalkylene-bridged polysilsesquioxane doped with both Er+3 ions and CdSe nanoparticles for the development of new laser amplifier materials. In photoluminescent experiments, a significant enhancement in fluorescent intensity at 1540 nm has been obtained from the fluoroalkylene-bridged glass. Analysis by nuclear magnetic resonance indicates a dramatically enhanced degree of condensation and a low level of hydroxyl environment in the fluoroalkylene-bridged glass matrix. The presence of CdSe nano-particles, by virtue of their low phonon energy, also appears to significantly influence the nature of the surrounding environment of Er+3 ions in those modified silicate systems, resulting in the increased fluorescent intensity.

#### V5.4/FF5.4

PL Excitation Mechanism of Eu and Pr doped GaN Grown by Hydrate Vapor Phase Epitaxy on Sapphire. Wojciech M. Jadwisienczak<sup>1</sup>, Henryk J. Lozykowski<sup>1</sup> and Richard J. Molnar<sup>2</sup>; <sup>1</sup>School of EECS, Ohio University, Athens, Ohio; <sup>2</sup>Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts.

We report measurements of the photoluminescence excitation (PLE) spectra, time resolved spectra and kinetics using tunable Sunlight laser system for Eu and Pr doped GaN. Investigated samples grown by hydrate vapor phase epitaxy were implanted with different rare earth ions doses and thermally treated at 1100 C in NH3 and N2 to remove ion implantation-induced damages, and make RE impurities optically active. From PLE experiments we have founded that the defect level near conduction band of GaN Eu doped samples are involved in an energy transfer to 4f electrons of Eu3+ ion. On the basis of experimental results the possible excitation mechanisms for RE3+ ions are briefly discussed.

## V5.5/FF5.5

Fabrication of Er3+/Pr3+ Co-Doped Soda Lime Glass Thin Films Using RF Magnetron Sputter and Optical Property Characterization. Sang Hoon Shin, Ki Young Yoo, Dong-ryul Jung, Jong Ha Moon and Jin Hyeok Kim; Department of Materials Science & Engineering, Chonnam National University, Gwangju, South Korea.

Er3+/Pr3+ co-doped soda lime glass thin films have been fabricated using RF magnetron sputtering method and their structural and optical properties have been studied. Deposition rate, crystallinity, and composition of glass thin films were investigated by scanning electron microscopy, transmission electron microscopy, and electron probe micro area analysis. Refractive index, birefringence, and binding characteristics between atoms have been investigated using a prism coupler and x-ray photoelectron spectroscopy. Er3+/Pr3+ co-doped soda lime glass thin films were prepared by changing substrate temperature (room temperature - 550°C), RF power (90W -150W), and Ar/O2 gas flow ratio at processing pressure of 4mTorr. The deposition rate depends on the processing parameters. It increased as the RF power increased and decreased as the Ar/O2 gas flow ratio increased. Especially, a high quality glass thin films that have similar composition with the compositions of the targets were obtained at 350°C, RF power of 130W, and gas flow ratio of Ar:O2 (40:0) with maximum deposition rate of  $1.6\mu\mathrm{m}/\mathrm{hour}$ . Refractive index increased from 1.5614 to 1.5838 and birefringence increased from 0.000154 to 0.000552 as the content of Pr increased. Binding energy of rare earth ions increased as the content of Pr increased.

#### V5.6/FF5.6

A Novel Approach to Achieve Broadband Luminescence from  $Tm^{3+}$  and  $Er^{3+}$  Codoped  $Al_2O_3$  Thin Films. Zhisong Xiao<sup>1</sup>, Rosalia Serna<sup>1</sup>, Carmen N. Afonso<sup>1</sup> and Ian Vickridge<sup>2</sup>; <sup>1</sup>Instituto de Optica, CSIC, Madrid, Spain; <sup>2</sup>Groupe de Physique des Solides, Universite de Paris 6 et 7, Paris, France.

Integrated optoelectronic circuits require the development of light sources and optical amplifiers in planar waveguides. Rare earth (RE) doping of dielectrics allows preparing suitable materials for these applications. Moreover, there is a great effort to develop devices for wavelength-division-multiplexing (WDM) in local network systems, and induces a demand for optical amplifiers utilized near 1.4  $\mu m$  and 1.6  $\mu m$ , in addition to the present silica-based erbium (Er) doped amplifiers (1530-1600 nm). Thus it is interesting to explore the possibility of profiting from emission of more than one kind of RE ion in a single integrated device. Tm<sup>3+</sup> is promising as a complement to  ${\rm Er}^{3+}$  (emission at 1.54  $\mu{\rm m}$ ) due to its emission bands around 1.47  $\mu{\rm m}$ and 1.6-1.8  $\mu$ m. In particular recently work we have found in Tm<sup>3</sup> doped  $Al_2O_3$  two efficient emission bands peaked at 1.48  $\mu m$  and 1.64  $\mu$ m. The aim of this work is to achieve the broadband luminescence by codoping thin films with Er<sup>3+</sup> and Tm<sup>3+</sup> and controlling both concentration and dopant distribution in the nanoscale. The amorphous aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) thin films codoped with Er<sup>3+</sup> and  $\mathrm{Tm}^{3+}$  have successfully been prepared by pulsed laser deposition (PLD). The number of Tm-Tm layers between two Er layers separated of nm has been designed to be 1, 2, and 5 corresponding to the film with Tm<sup>3+</sup>-Tm<sup>3+</sup> layer in-depth separation of 3, 2 and 1 nm, and an areal density of Tm<sup>3+</sup> in the range of 2.15×10<sup>15</sup> - 1.07×10<sup>16</sup> cm<sup>-2</sup> is determined by the RBS analyses. Er<sup>3+</sup> areal density is \$\inp 2.15×10<sup>15</sup> cm<sup>-2</sup> for all Er-Tm doped films. When pumping with 794 nm light from a Ti: sapphire laser a broad photoluminescence (PL) band with a full-width half maximum (FWHM) up to 250 nm was observed. This broad PL band is the result of the convolution of simultaneous luminescence of both  $\rm Er^{3+}$  and  $\rm Tm^{3+}$ . By the addition of  $\rm Tm^{3+}$  the typical  $\rm Er^{3+}$  spectrum in Al<sub>2</sub>O<sub>3</sub> peaked at 1540 nm (FWHM \$ $\sim$  60 nm) was modified by an enhancement of the PL intensity in the region of 1400-1500 nm and the appearance of a broad shoulder peaked at 1640 nm. The evolution of the broad band spectra was studied as a function of the  ${\rm Tm}^{3+}/{\rm Er}^{3+}$  concentration ratio. As the concentration ratio increases both the PL intensity and lifetime of 1640 nm peak increase, and in the meantime both the PL intensity and lifetime of 1540 nm peak decrease. It is shown that this is the consequence of energy transfer between the transition of  ${\rm Er}^{3+}$ :  ${}^4{\rm I}_{13/2}$ -  ${}^4\mathrm{I}_{15/2}$  and  $\mathrm{Tm}^{3+}$ :  ${}^3\mathrm{F}_4$  -  ${}^3\mathrm{H}_6$ . It will be shown how by adjusting the Tm content and Tm-Tm separation between two Er layers can be used to tailor 1.4-1.7  $\mu m$  PL response of Er-Tm codoped Al<sub>2</sub>O<sub>3</sub> films for broadband application.

## V5.7/FF5.7

The Impact of Deposition Parameters on Optical and Compositional Properties of Er Doped SRSO Thin Films Deposited by ECR-PECVD. Michael Flynn<sup>1,2</sup>, Jacek Wojcik<sup>1,2</sup>, Edward Irving<sup>1,2</sup> and Peter Mascher<sup>1,2</sup>; <sup>1</sup>Engineering Physics, McMaster University, Hamilton, Ontario, Canada; <sup>2</sup>Centre for Electrophotonic Matrials and Devices, Hamilton, Ontario, Canada.

Silicon rich silicon oxide (SRSO) thin films have been deposited, with in-situ Er doping via an organometallic precursor, using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD). The films had thicknesses of approximately 1000? and silicon concentrations ranging from 33 to 45 %. Using heavy ion elastic recoil detection, it was found that the SRSO composition, specifically the silicon to oxygen ratio, was significantly impacted by the erbium incorporation. It was also determined that varying the microwave power affects the incorporation of erbium during the thin film deposition process. Additionally, ellipsometry has been used to characterize the effects of microwave power and film composition on the optical properties of the films. Results from Fourier transform infra-red absorption measurements of these films will be discussed in relation to the composition and optical measurements and with reference to the broader field of silicon based photonics. This work is being supported by Ontario Centres of Excellence (OCE) Inc. and the Ontario Photonics Consortium (OPC).

## V5.8/FF5.8

Luminescence of Rare Earth Doped Si/ZrO<sub>2</sub> Co-Sputtered Films. <u>Carlos Rozo Rozo</u>, Luis Fonseca, Oscar Resto and Zvi Weisz; Physics, University of Puerto Rico at Rio Piedras, San Juan, Puerto Rico.

 ${\rm Er}^{3+}$ ,  ${\rm Nd}_{3+}$  and  ${\rm Tm}_{3+}$  doped  ${\rm Si/ZrO}_2$  thin films have been prepared by rf co-sputtering. The films are 5 inches long and divided into 50 sections or positions, labeled from P1 to P50. The target

configuration is such that the main target is ZrO<sub>2</sub> (182.14 cm<sup>2</sup>), the rare earth (RE) oxide pellet (1.4 cm<sup>2</sup>) is placed on the main target below the middle of section of the film and the Si chip (6.67 cm placed on the main target below one end of the film (P40 to P50). The films were annealed to 700°C. The  ${\rm Er^{3+}}~^4I_{13/2} \rightarrow ^4I_{15/2}$  emission was detected but unlike similar Er-doped Si/SiO<sub>2</sub> and Er-doped Si/Al<sub>2</sub>O<sub>3</sub> films no  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  emission was detected. The  ${}^4\mathrm{I}_{13/2} o {}^4\mathrm{I}_{15/2}$  emission shows a much narrower peak at 1527 nm (FWHM  $\approx 7 \text{nm}$  for P20) with two weaker side bands from 1430 mm to 1500 nm and from 1550 nm to 1600 nm. The  ${\rm Nd}^{3+} {}^4{\rm F}_{3/2} \to {}^4{\rm I}_{9/2}, {}^4{\rm F}_{3/2} \to {}^4{\rm I}_{11/2},$  and  ${}^4{\rm F}_{3/2} \to {}^4{\rm I}_{13/2}$  emissions were detected being the  ${}^4{\rm F}_{3/2} \to {}^4{\rm I}_{11/2}$  peaked at 1065 nm (FWHM  $\approx$  40 nm for P30) the strongest. The  ${}^4{\rm F}_{3/2} \to {}^4{\rm I}_{9/2}$  emission is relatively weak, less than one-fourth the peak intensity of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  emission but is broad (FWHM  $\approx 80$  nm for P30). Compared to similar Nd-doped Si/SiO $_2$  and Nd-doped Si/Al $_2$ O $_3$  films the  $^4{
m F}_{3/2} 
ightarrow \, ^4{
m I}_{13/2}$ is stronger, peaked at 1324 nm and extending from 1280 nm to 1380 nm. No  $\rm Er^{3+}\,^4I_{13/2} \rightarrow ^4I_{15/2}$  emission or Nd<sup>3+</sup>  $^4F_{3/2}$  emissions were detected for the Si rich ends of the respective films, being the emission stronger from the Si poor end of the film towards the middle of the film. The maximum  ${\rm Er}^{3+}\,^4{\rm I}_{13/2} \rightarrow ^4{\rm I}_{15/2}$  emission is for P20 and the maximum peak intensity for the Nd<sup>3+</sup>  $^4{\rm F}_{3/2} \rightarrow ^4{\rm I}_{11/2}$  emission is for P30. The excitation wavelength dependence behavior for the Nd<sup>3+</sup>  $^4F_{3/2} \rightarrow ^4I_{11/2}$  emission is that typical of energy transfer from the Si nanoparticles to the emitting Nd<sup>3+</sup> ions. The excitation wavelength behavior for the Er<sup>3+</sup>  $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$  emission reflects a mix of energy transfer from the Si nanoparticles and strong resonant absorption for excitation wavelengths of 488.0 nm and 514.5 nm. The  $\rm Tm^{3+}$  doped Si/ZrO $_2$  thin film does not exhibit infrared (IR) PL from the  $^3H_4 \rightarrow ^3F_4$  emission or the  $^3F_4 \rightarrow ^3H_0$  emission. The intense band from 500 nm to 800 nm observed for all of the RE doped Si/ZrO<sub>2</sub> films, due to defects in ZrO<sub>2</sub>, barely permits the detection of the Tm<sup>3+</sup>  $^3H_4 \rightarrow ^3I_6$  emission which is best observed for P35.

> SESSION V6: Spectroscopy and New Materials Chairs: Minoru Fujii and Zakhary Krasilnik Thursday Morning, March 31, 2005 Room 2009 (Moscone West)

#### 8:30 AM \*V6.1

1.4-1.7  $\mu$ m Band Emission Properties of Tm<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub> Thin Films. Rosalia Serna<sup>1</sup>, Zhisong Xiao<sup>1</sup>, Carmen N. Afonso<sup>1</sup> and Ian Vickridge<sup>2</sup>; <sup>1</sup>Instituto de Optica, CSIC, Madrid, Spain; <sup>2</sup>Groupe de Physique des Solides, Universite de Paris 6 et 7, Paris, France.

As a result of the rapid increase in information traffic, there is a demand of broadband optical amplification beyond the conventional band of 1530-1600 nm (C+L-band) developed by erbium-doped fiber amplifiers (EDFAs). A logical extension of EDFAs would be the addition of other rare-earth (RE) ions. Tm<sup>3+</sup> is interesting among various RE ions because it gives rise to various luminescence bands in the visible and infrared regions, the latter being in the desired wavelength range of the fiber communication (1400-1700 nm). Nevertheless, it has been found that one of the levels of interest of  $\mathrm{Tm}^{3+}$  ( ${}^{3}\mathrm{H}_{4}$ ) is easily quenched in a high phonon energy host material such as silica glass ( $\$\sim1100~{\rm cm}^{-1}$ ). This problem can be circumvented by use of low phonon energy materials like fluoride glass  $(\$\sim580~\mathrm{cm}^{-1})$  and some multicomponent glasses. However, these materials present some disadvantages as they are expensive and their mechanical and thermal properties are far from those offered by silica-based glasses. For waveguide devices there is an attractive alternative based on the use of amorphous aluminum oxide ( $\mathrm{Al}_2\mathrm{O}_3$ ). The development of waveguide technology has been explored as the high contrast between the refractive index of  $Al_2O_3$  and that of the  $SiO_2$  cladding layer (\$ $\sim$ 0.2) leads to a high confinement of the guided light, making possible smaller device structures. Furthermore, it has excellent thermal stability and the maximum phonon energy of 870 cm<sup>-1</sup>. Nevertheless, as far as we know the Tm<sup>3+</sup> emission in this material has not been reported. In this paper, we will show a nanostructured approach to prepare  $\rm Tm^{3+}\text{-}doped~Al_2O_3$  thin films by pulsed laser deposition (PLD). Two broad emission bands peaked at  $1.48~\mu\mathrm{m}$  and  $1.64~\mu\mathrm{m}$ , originating from the transition of  $\mathrm{Tm}^{3+}$ :  ${}^{3}\mathrm{H}_{4}$  - ${}^{3}\mathrm{F}_{4}$  and  ${}^{3}\mathrm{F}_{4}$  -  ${}^{3}\mathrm{H}_{6}$ , are observed when pumping with 794 nm light from a Ti: sapphire laser. The photoluminescence (PL) intensity was studied as function of annealing temperature and Tm<sup>3</sup> concentration. It is shown that The PL intensity increases with the increase of the annealing temperature and Tm<sup>3+</sup> concentration. However, it will be shown that concentration quenching effect and cross-relaxation can result in a reduction of the PL intensity with the  ${\rm Tm^{3+}}$  concentration above  $4{\times}10^{20}~{\rm cm^{-3}}$ . Since the transition of  ${\rm Tm^{3+}}$ :  ${\rm ^3H_4}$  -  ${\rm ^3F_4}$  has clearly been observed and is not quenched as in high phonon energy materials, we conclude that  ${\rm Tm^{3+}}$ :  ${\rm Al_2O_3}$  is a

very promising material for the development of optical waveguide amplifier in the range of 1.4 - 1.7  $\mu m.$ 

9:00 AM <u>V6.2</u>

Gallium Oxide as a Host for Rare Earth Elements. John Muth, Christian Mion, Anuj Dhawan and Jason Kekas; ECE Dept Box 7911, NC State University, Raleigh, North Carolina.

Using Pulsed Electron Beam and Pulsed Laser Deposition single crystal  $\beta$ -Ga2O3 was grown epitaxially on double side polished c-axis oriented sapphire substrates. The resulting films were smooth with RMS surface roughness by AFM of about 1 nm. Prism coupling was used to obtain the refractive index of 1.93 at 632 nm resulting in a natural planar waveguide. The wide band gap of 4.9 eV suggests that the films could be a suitable host for rare earth elements. Optical waveguiding, cathodoluminescence and optical transmission measurements of rare earth doped Gallium Oxide films on sapphire will be presented.

9:15 AM V6.3

Rare-Earth Doped Chalcogenide Thin Films for Photonic

Application by Excimer Laser Ablation.

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Chalcogenide glasses have been extensively studied as host media for rare-earth (RE) doped photonic devices due to potential application as optical amplifiers for optical telecommunication. However, fabrication of RE doped homogeneous thin films of chalcogenide glass systems is a difficult task. The composition of the films usually deviates from that of the source material and depends on the method and conditions of the film deposition technique. Doping high amounts of RE atoms (1 to 2 at%) using conventional preparation methods such as glass quenching or physical vapor deposition techniques often results in physical or chemical clustering of the RE atoms in the glass matrix also. The respective evaporation rates of chalcogenide glass and rare-earth atoms are so different that vacuum evaporation of doped bulk glass leads to nearly undoped films. In this paper, we report the deposition and properties of RE doped chalcogenide films fabricated by pulsed laser deposition (PLD), using 15 ns KrF laser pulses at various laser energy densities and substrate temperatures. This method was used in order to take advantage of its ability to create homogenous films with complex compositions. We have used the PLD technique to fabricate Er3+ and Nd3+ doped chalcogenide glasses of different compositions. The composition of the bulk and respective thin film samples was determined by Wavelength Dependence X-ray analysis (WDX). The optical constants of the deposited films were determined by analyzing transmission spectra obtained using a spectrophotometer. The photoluminescence (PL) of the films was studied using a set of laser diodes operating at different wavelengths. We examined the effects of changing the substrate temperature during deposition on the optical constants and photoluminescence.

9:30 AM <u>V6.4</u>

Infrared Electroluminescence from Zinc Sulfide Doped with Rare Earth Fluorides. Avni A. Argun<sup>1</sup>, David M. DeVito<sup>1</sup>, Ajay Kale<sup>1</sup>, William Glass<sup>1</sup>, Mark Davidson<sup>2</sup> and Paul H. Holloway<sup>1,2</sup>; Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>MICROFABRITECH, University of Florida, Gainesville, Florida.

Thin film electroluminescent (EL) devices serve as an excellent design for high efficiency infrared emitters. A variety of applications exist for infrared emitters including chemical analysis, infrared displays, communications, and therapeutic treatment. Rare earth elements, such as Erbium, Neodymium, and Holmium are ideal choices for phosphors because of the many sharp transitions they possess in the visible region from 500-700 nm and in the infrared region from 850-2800 nm. Zinc sulfide (ZnS) is a suitable host material as it provides a stable wide band gap of 3.6 eV at 300K in which the electrons can be excited to adequate energies to produce emission from rare earth dopants. Thin films of rare-earth doped ZnS were RF  $\,$ magnetron sputter deposited at 120W and 160 °C deposition temperature from dual targets of an undoped ZnS and a rare-earth fluoride doped ZnS with varying duty cycles. Suppression of visible wavelengths is desirable and can result in enhanced near infrared emission and emergence of new transitions at longer wavelengths. This is achieved by post-deposition annealing of thin film phosphors at temperatures between 350 °C and 525 °C under  $\rm N_2$  for 1 h. As an example, the maximum EL radiance for ZnS:ErF<sub>3</sub> at 1550 nm has increased from  $\sim 1 \mu \text{W/cm}^2$  (pre-anneal) to  $28 \mu \text{W/cm}^2$  (post-anneal). Achieving optimum brightness and selective wavelength emission require proper concentrations of both rare-earth ion and fluorine

which were determined by EDS and SIMS analysis.

9:45 AM <u>V6.5</u>

Erbium-doped Amorphous-Si-C-O matrix (a-SiC $_x$ O $_y$ :Er) - A Novel Silicon-Based Material for Near-Infrared Optoelectronic Applications. Spyros Gallis<sup>1</sup>, Mengbing Huang<sup>1</sup>, Vasileios Nikas<sup>1</sup>, Harry Efstathiadis<sup>1</sup>, Eric Eisenbraun<sup>1</sup>, Alain E. Kaloyeros<sup>1</sup>, Jessica Freeman<sup>2</sup>, Ei Ei Nyein<sup>2</sup> and Uwe Hommerich<sup>2</sup>; <sup>1</sup>College of Nanoscale Science and Engineering, The University at Albany-SUNY, Albany, New York; <sup>2</sup>Department of Physics, Hampton University, Hampton, Virginia.

Due to its low-k dielectric value, and excellent mechanical and chemical properties, amorphous silicon oxycarbide ( $SiC_xO_y$ ) has recently received much attention in copper interconnect- related applications. In this work, we demonstrate that  $\mathrm{SiC}_x\mathrm{O}_y$  material can also be an excellent host matrix for erbium (Er)- doped silicon-based optoelectronics. Amorphous- $SiC_xO_y$  (a- $SiC_xO_y$ ) materials were synthesized via thermal chemical vapor deposition (TCVD) at 800°C using a single source oligomer, 2,4,6-trimethyl-2,4,6-trisila-heptane (C<sub>7</sub>H<sub>22</sub>Si<sub>3</sub>) and oxygen (O<sub>2</sub>). By carefully modulating the flow rate of oxygen, the  $SiC_xO_y$  thin film composition could be controlled, resulting in  $SiC_xO_y$  films with varying carbon (x) and oxygen (y) compositions in the range of 0 - 1.71. The resulting  $SiC_xO_y$  samples along with a SiO<sub>2</sub> sample were implanted with Er ions at 260 keV to a dose of  $1\times10^{15}$  /cm<sup>2</sup>. Following post-implantation annealing at 900°C, room temperature photoluminescence (PL) measurements were performed under both ultra-violet (wavelength range 336-363 nm) and visible light (wavelength 496.7 nm) excitations to monitor the intra-4f transition of doped Er ions. The chemical and structural characteristics of  $SiC_xO_y$  were also characterized utilizing various analytical techniques including ion scattering, transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The Er-doped  $\mathrm{SiC}_x\mathrm{O}_y$  materials exhibited a strong room-temperature PL at  ${\sim}1532$ nm wavelength. Furthermore, the infrared PL intensity was found to be highly dependent on the compositions of carbon and oxygen, while the strongest luminescence emission was obtained from an Er-doped  $SiC_{0.49}O_{1.09}$  thin film. The data suggested that a white light source or light emitting diode can be used as the pump for exciting Er in Si-C-O materials. In comparison with Er-doped SiO<sub>2</sub>, the PL intensity from Er-doped SiC $_{0.49}$ O $_{1.09}$  was enhanced by factors of  $\sim\!23$  and  $\sim\!14$  under, respectively, UV and visible light excitations. The enhanced performance observed herein is comparable with those reported in previous work that used Si nanocrystals as Er sensitizers in silicon oxide. Neither Si nor SiC nanoclusters were seen in the  $SiC_xO_y$ samples grown under the above-mentioned processing conditions. In this context, the efficient infrared Er-related luminescence was correlated to the elemental composition and chemical bonding of the  $\mathrm{SiC}_x\mathrm{O}_y$  films. The work by the present investigators thus presents a novel approach for achieving efficient infrared luminescence emission from Er ions through engineering the structures of Si-C-O networks.

10:30 AM V6.6

A New Photoluminescence Band in Hafnium-implanted Silicon. Ravinder Sachdeva<sup>1</sup>, Andrei A. Istratov<sup>1</sup>, Prakash Deenapanray<sup>2</sup> and Eicke R. Weber<sup>1</sup>; <sup>1</sup>Material Science and Engineering, U.C. Berkeley, Berkeley, California; <sup>2</sup>Center for Sustainable Energy Systems, The Australian National University, Canberra.

A new photoluminescence (PL) band in the energy range of 700 meV to 950 meV associated with hafnium implanted in silicon is reported. Activation of the Hf-optical centers requires a 1000C anneal step. The intensity of the PL lines appear to depend on the cooling conditions. The spectrum consists of five peaks in the rapidly quenched sample as opposed to twenty one in the slow cool sample. The peak with the highest intensity is found in the rapidly quench sample at 943.8meV with two phonon replicas. Temperature and excitation power dependent PL are performed on this peak. It is also found that oxygen coimplantation enhances the PL intensity. A shift in the position of photoluminescence peaks observed on the samples implanted with two different isotopes of Hf confirms the Hf-related origin of the observed photoluminescence band.

10:45 AM <u>V6.7</u>

Lattice Location of Rare Earth Ions in Semiconductors: Interpretation and Limitations of using g Values. David Carey, University of Surrey, Guildford, United Kingdom.

The g values of rare earth ions obtained from either paramagnetic resonance or Zeeman measurements are often used to interpret the local structure surrounding the rare earth ion. In the case of centers with cubic symmetry the g value can be used to distinguish between substitutional and interstitial sites. For centers with less than cubic symmetry the average g value, taken as 1/3 trace of the g tensor, is often used as a indication of the lattice location and/or a measure of the strength of the local crystal field. This approach has been widely used but is based on the assumption that the non-cubic terms to the crystal field potential are small compared to the cubic crystal field. In this paper we have explored this assumption by calculating the principal g values for a range of non-cubic crystal fields for the Er3+ion. We determine the limits over which the average g value approach is valid and other effects, should as the reduction in the g values due covalence effects, are also discussed. Comparison is made with published results from paramagnetic resonance and Zeeman measurements.

#### 11:00 AM V6.8

UV Excitation Mechanism of Rare Earth Ions in AlN. Henryk J. Lozykowski<sup>1</sup>, Wojciech M. Jadwisienczak<sup>1</sup>, Abdelhak Bensaoula<sup>2</sup>, Chris Boney<sup>2</sup> and Otton Monteiro<sup>3</sup>; <sup>1</sup>School of EECS, Ohio University, Athens, Ohio; <sup>2</sup>Nitride Materials & Device Laboratory, University of Houston, Houston, Texas; <sup>3</sup>Lawrence Berkeley National Laboratory, University of California, Berkeley, California.

We report measurements of the luminescence properties and excitation mechanism of RE ions implanted into AlN films grown by plasma source molecular beam epitaxy. Investigated samples were implanted with Pr, Eu, Tb and Tm ions at room temperature and thermally activated at a temperature of 1050 C in N2 or NH3 to remove ion implantation-induced damages, and make RE impurities optically active. The PL measurements were performed using a He-Cd laser, Sunlight laser (pulse operating), and tunable light source utilizing a Xenon high pressure lamp with double grating monochromator. The high-resolution photoluminescence (PL) and photoluminescence excitation (PLE) measurements have been carried out in temperature range from 13 K to 300 K. These studies shown that under below bandgap excitation all investigated samples shown well-defined visible emissions due to intra 4f-shell transitions of the RE3+ ions. The PLE spectra have revealed several excitation bands in the 200 nm - 360 nm spectral range. Finally, on the basis of experimental results the possible excitation mechanisms of RE3+ ions are briefly discussed.

## 11:15 AM <u>V6.9</u>

A New Method to Produce Rare Earth-Doped Gallium Nitride Phosphor Powders. <u>Gustavo A. Hirata</u><sup>1,2</sup>, Jonathan H. Tao<sup>1</sup>, Po Yu Chen<sup>1</sup>, Kailash C. Mishra<sup>3</sup> and Joanna McKittrick<sup>1</sup>; <sup>1</sup>MAE, UCSD, La Jolla, California; <sup>2</sup>CCMC-, UNAM, Ensenada, Baja California, Mexico; <sup>3</sup>Central Research, OSRAM Sylvania, Beverly, Massachusetts.

We report on the fabrication and luminescent properties of rare earth-doped gallium nitride (GaN) phosphor powders. Single phase GaN and GaN:RE3+ powders were prepared by using a novel chemical route. Traditionally, GaN powders are produced by placing Ga or Ga2O3, or one of the Ga halides in an ammonia flow. However, the formation of a GaN layer on the surface prevents further reaction, resulting in poor crystallinity and contaminated powders [1]. Precursors such as [H2GaNH2]3 and Ga(GaC2H5)NH3, can be thermally decomposed to produce GaN nanocrystals but these materials show traces of carbon [2]. Solid state displacement reactions have been carried out to synthesize polycrystalline GaN using GaI3 and Li3N under high pressure (4.5 GPa), and to synthesize GaN nanocrystals using GaCl3 and Li3N in a hot benzene solution with pressure [3]. In this work a new method for the synthesis of high purity, single phase doped GaN powders is reported. (Ga1-xREx)N and (Ga1-xTMx)N powders are obtained by dissolving metal nitrates (Ga(NO3)3, (RE(NO3)3, TMz+(NO3)z) in deionized water with ammonium hydroxide in order to form a gallium/RE or gallium/TM hydroxide. The hydroxide powders are then reacted with ammonium fluoride to form ammonium hexafluoroRE-gallate or hexafluoroTM-gallate. The dried hexafluorate powders are placed in a boron nitride crucible and reacted at 1200°C in a high purity N2 flow followed by a NH3 flow. X-ray diffraction analysis showed that single phase GaN powders are formed. Preliminary results show (Ga0.95Eu0.05)N powders to be luminescent, with the main emission occurring at 613 nm from the 5D0?7F2 transition of the Eu3+. High-purity GaN powders are obtained according to X-ray photoelectron spectroscopy (XPS) chemical analysis. HRTEM performed on single crystals with hexagonal (wurzite) structure showed small cubic domains (zincblende) and a high density of stacking faults, all aligned along the [0001] and <111> directions, respectively. These powders were used to fabricate targets for thin film deposition studies. This method can be used to obtain red-luminescence GaN:Eu3+ and other rare earth (e.g. Er, Tb, Tm)-doped GaN powders to produce green and blue luminescence as well. A more detailed discussion of these new RE-doped GaN materials will be presented at the conference. 1. A. Addamiano, J. Electrochem. Soc. 108, 1072 (1961). 2. J.W. Hwang, J.P. Campbell, J. Kozuboowski, S.A. Hanson, J.F. Evans and W.L. Gladfelter, Chem. Mater. 7, 517 (1995). 3. Y. Xie, Y. Qian, W. Wang, S. Zhang & Y. Zhang, Science 272, 1926 (1996).

## 11:30 AM <u>V6.10</u>

Visible Light Emission from Er:GaN and Eu:GaN Powder. Huaqiang Wu<sup>1</sup>, Janet Hunting<sup>2</sup>, Carl B. Poitras<sup>1</sup>, Michal Lipson<sup>1</sup>, Francis J. DiSalvo<sup>2</sup> and Michael G. Spencer<sup>1</sup>; <sup>1</sup>School of Electrical and Computer Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Department of Chemistry & Chemical Biology, Cornell University, Ithaca, New York.

We report on the first demonstration of rare earth elements doping in GaN power at high temperature. The recent demonstration of visible (blue, green, red) and infrared (1.54 $\mu$ m) electroluminescence from rare earth (RE) doped GaN brings significant interest to this class of materials for possible applications in optical communications and full color displays.<sup>1–3</sup> In these works, the incorporation of RE atoms into GaN is achieved by either in situ epitaxial growth with the GaN layer or ion-implantation after the layer growth step. Although extensive work has been done on doping GaN in bulk form with RE, few studies have been done on doping GaN in a powder form with RE. In our work, RE is successfully incorporated into GaN powder through the reaction between molten (Ga+RE) and NH<sub>3</sub> at 1000°C using Bi as a wetting agent. Photo excitation with an Ar and UV laser results in strong visible light emissions from two narrow lines at 537 and 558 nm identified as Er transitions from the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels to the  $^4\mathrm{I}_{15/2}$  ground state in the Er doped GaN powder sample. Red emission at 623nm corresponding to transition  $^5\mathrm{D}_0$  to  $^7\mathrm{F}_2\mathrm{has}$  also been achieved from Eu doped GaN powder. X-ray diffraction shows that both structures of the GaN powder doped with Er and Eu are the wurtzite structure. Microprobe analysis reveals that Er or Eu is distributed evenly in the powder particles. These rare earth doped GaN powders are used to make thin film on Si, glass and sapphire substrates. Continuous and highly oriented films showed good luminescence properties. Structure, morphology, Cathodoluminescence and photoluminescence characterizations have been carried out on these films. Electroluminescence measurements are carrying out and will be reported during the meeting. <sup>1</sup>A. J. Steckl and J. M. Zavada, Mater. Res. Bull. 24, 33 (1999). <sup>2</sup>J. M. Zavada and D. Zhang, Solid-State Electron. 38, 1285 (1995). <sup>3</sup>A. J. Steck, J. C. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Wang, and R. Jones, IEEE J. Selected Topics in Quantum Electronics, 8, 749 (2002).

## 11:45 AM <u>V6.11</u>

How to Make Algae Glow in the Dark. Michael Weatherspoon, Shawn Michael Allan, Ye Cai, Jeffrey King, Christopher Summers and Kenneth Sandhage; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Intense global activity to produce micro-to-nanoscale devices with well-controlled structures for optoelectronic applications has led to appreciable interest in three-dimensional (3-D) self-assembly processes. Elegant examples of self-assembly can be found in nature. Certain biomineralizing micro-organisms are adept at mass-producing 3-D micro-structures with genetically precise morphologies. An exceptional variety of silica-based structures are generated by aquatic micro-algae known as diatoms. Diatoms are single-celled organisms that assemble microshells (frustules) comprised of silica nanoparticles. While the tens of thousands of extant diatom species present on the planet provide a rich variety of frustule shapes for devices, the range of potential applications is severely limited by the natural silica-based chemistry. We demonstrate here how a sol-gel coating technique can be used to convert such biogenic silica-based structures into luminescent (non-silica-based) rare-earth-doped materials while preserving the intricate 3-D shapes and features. Europium-doped BaTiO3-based replicas have been synthesized using a multi-step process consisting of: i) reactive conversion of the silica scaffold into a chemically-compatible substrate and ii) application of an alkoxide-derived coating that is then fired to form the desired multicomponent luminescent ceramic phase. Eu-doped BaTiO3-based frustules exhibited a bright red luminescence upon exposure to 337 nm stimulation. This shape-preserving chemical conversion approach may also be applied to a wide variety of other self-assembled 3-D biogenic structures. Potential applications for such luminescent, biologically-assembled micro/nanostructures will be discussed.