

SYMPOSIUM J

Materials Engineering for Solid-State Lighting

November 25 – 27, 2001

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TUTORIAL

FT J: INTRODUCTION TO SOLID STATE LIGHTING

Sunday, November 25, 2001
1:30 p.m. - 5:00 p.m.
Room 203 (Hynes)

Estimated total global consumption of electricity is about 1×10^{13} kW-h per year with 21% of that consumed for lighting. Thus, an improvement of luminous efficiency by 1% may save 2 billions dollars per year. An introduction of new, efficient light sources with high color rendering indices is thus of high importance for energy saving. In his article on solid-state lighting, Nick Holonyak, Jr. stated "... it is vital to know that the LED is an ultimate form of lamp, in principle and in practice, and that its development indeed can and will continue until all power levels and colors are realized." This tutorial on solid-state lighting will cover the following issues: historical survey, vision, photometry and colorimetry, bulbs and tubes, lighting, economy of lighting, light-emitting diodes (LEDs), generation of light, extraction of the light from LEDs, white LEDs, UV LEDs, and present and future applications.

Instructors:

Remis Gaska, Sensor Electronic Technology, Inc.
Artūras Zukauskas, Vilnius University
Michael S. Shur, Rensselaer Polytechnic Institute

SESSION J1: INORGANIC MATERIALS FOR SOLID-STATE LIGHTING I

Chair: Jeffrey S. Nelson
Monday Morning, November 26, 2001
Room 301 (Hynes)

8:30 AM *J1.1

PROGRESS IN HIGH POWER, HIGH EFFICIENCY, LONG LIFE SOLID STATE LIGHTING SOLUTIONS. Paul S. Martin, LumiLeds Lighting, San Jose, CA.

LumiLeds recent advances in AlInGaP device design, AlInGaP device design high power packaging and phosphor conversion technology have brought LEDs into new markets for solid state lighting. These markets require high flux density, high efficiency and high reliability the traditional 5 mm LED cannot provide. This talk will describe recent advances in red, green and white LEDs that surpass the 100 lm/LED benchmark and illuminate a path into the future for solid state lighting.

9:00 AM *J1.2

OPTIMIZATION AND MANUFACTURABILITY OF SHORT WAVELENGTH BLUE, VIOLET AND ULTRAVIOLET AlGaInN LEDs FOR WHITE LIGHT APPLICATIONS. Mary H. Crawford, Kevin C. Baucom, Christian Wetzel, Winston V. Schoenfeld, Vishwanath Krishnamoorthy, Eric C. Bretschneider, Christopher J. Eiting, Michael G. Brown, Jeffrey S. Nelson, Uniroyal Opto-electronics, Tampa, FL.

Semiconductor-based light emitting diodes (LEDs) have made strong inroads into monochrome applications such as signal lighting and displays, however more development is needed to make a substantial impact on white lighting applications. The primary limiting factor at this time is the relatively low efficiency of commercial white LEDs. One method to generate white light involves the use of blue or near-UV InGaN LEDs in conjunction with wavelength conversion materials such as phosphors. In this talk, we present the optimization and performance of near-UV to blue wavelength LEDs (380 nm-460 nm) for the specific application of phosphor-based white lighting. Our main focus will be to compare material and device performance trade-offs as a function of emission wavelength. Critical manufacturing issues such as device yield and reliability will also be addressed.

9:30 AM J1.3

HIGH POWER ULTRAVIOLET LIGHT EMITTING DIODES AT 340 NANOMETERS USING QUATERNARY AlInGaN MULTIPLE QUANTUM WELLS. V. Adivarahan, A. Chitnis, J.P. Zhang, M. Shatalov, J.W. Yang, G. Simin, M. Asif Khan, University of South Carolina, Dept. of Electrical Engineering, Columbia, SC; R. Gaska, M.S. Shur, Sensor Electronic Technology Inc., Latham, NY.

An ultraviolet light emitting diode with peak emission wavelength at 340 nm is reported. The active layers for the device comprised of quaternary AlInGaN/AlInGaN multiple quantum wells, which were deposited over sapphire substrates using a new pulsed atomic layer epitaxy process. This novel approach of fabricating AlInGaN layers by

the repeats of a unit cell with atomic dimensions allows for a precise control of the composition and thickness. The device epilayer structures consisted of the active MQW surrounded by n- and p-type barrier and injection layers. Both the barrier types consisted of AlGaIn/AlGaIn superlattices to enhance conductivity and improve surface morphology. These epilayers were characterized using PL, X-ray, AFM and Hall measurements. Subsequently 300x300 um mesa etched LED structures were fabricated. Comparative study of devices over sapphire and SiC substrates was done in order to determine the influence of epilayer design on the performance parameters and the role of the substrate absorption. We were able to obtain powers as high as 0.12 mW at 340 nm with a FWHM of 15 nm. This points to an excellent potential of our quaternary active layers approach for deep UV LEDs. New device designs with much improved carrier confinement are being fabricated to further increase the emission powers. The influence of these new designs on emission properties will also be discussed.

9:45 AM J1.4

ELECTRON BEAM DISSOCIATION OF Mg-H CENTERS IN Mg-DOPED GaN. C.H. Seager, N.A. Missert, S.M. Myers, Sandia National Laboratories, Albuquerque, NM.

While it is known that minority carrier injection from n layers and direct injection of 10-20 keV electrons with an electron gun can create p-type conduction in as grown Mg-doped GaN, the details of this de-passivation process are poorly understood. We have studied this process by carefully controlling our electron beam uniformity, dose, and dose rate while accurately measuring both the infrared vibrational signature of Mg-H centers and the cathodoluminescence (CL) from MOCVD-grown GaN. We find that doses of the order of 8-10 mC/cm² reduce the optical absorption from this center by ~30%; however, much higher doses result in ~1/2 of the hydrogen still bonded at substitutional Mg sites. Concurrent with the electron beam exposures we find large changes in the CL spectra including a luminescence peak which is strongly correlated with H content and which displays a significant red shift as the de-passivation process evolves. We also observe that mild (500°C, 5 minute) thermal anneals restore the size of the Mg-H absorption, indicating that the e-beam debonded hydrogen has not left our samples. We will compare the rate of the electron beam debonding process for H and D containing GaN and use this information to speculate on the nature of the debonding process. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

10:30 AM *J1.5

III-NITRIDE MICRO-SIZE LIGHT EMITTERS FOR SOLID-STATE LIGHTING APPLICATIONS. H.X. Jiang and J.Y. Lin, Department of Physics, Kansas State University, Manhattan, KS.

Bright blue LEDs based on III-nitrides paved the way for full color displays and raised the possibility of mixing three primary colors to obtain white light for general illumination by semiconductor LEDs. The current main approach for achieving white light using LEDs is to use a phosphor to down-convert the emission from a blue or UV LEDs. In such an application, improving the LED efficiency is a key step. Most recently, we have succeeded in fabricating electrical pumped micro-size LEDs, as well as in interconnecting hundreds of these micro-size LEDs (size on the order of 10 microns in diameter) made from InGaIn/GaN QW light emitter structure. These interconnected microdisk LEDs fit into the same device area taken up by a conventional LED of about 300 x 300 μm². It was shown that the interconnected microdisk LEDs could boost the LED emission efficiency by more than 60%. It is believed that the novel device can overcome two biggest problems facing LEDs - the low extraction efficiencies due to the total internal reflection occurring at the LED/air interface and the problem of current spreading. Additionally, the strain induced piezoelectric field in the active quantum well regions may be reduced in micro-size LEDs, resulting in increased internal quantum efficiency. Furthermore, the processing steps of these interconnected micro-size LEDs are the same as those of the conventional broad-area LEDs. It is thus expected the manufacture yield of these novel interconnected micro-size LEDs to rival with the conventional LEDs. The present method of utilizing micro-size LEDs can be further developed to boost the LED emission efficiencies for solid-state lighting applications, as well as for UV light emitters to be used for chemical and biohazard substances detection.

11:00 AM *J1.6

ALTERNATIVE SUBSTRATES FOR GaN-BASED LEDs. T.J. Anderson, O. Kryliouk, M. Reed, M. Mastro and T. Dann, Chemical Engineering Department, University of Florida, Gainesville, FL.

The emergence of relatively high brightness GaN-based LEDs emitting in the blue and near-UV has encouraged their use in white

lighting applications. Further improvements in brightness and process yield, however, are necessary to realize broad commercialization. The large lattice and thermal mismatches between GaN and sapphire or SiC have motivated the investigation of alternative substrates. This presentation will focus on the growth of GaN on nearly lattice-matched LiGaO₂ and LiAlO₂ substrates, as well as growth on Si. We report on successful growth of single crystal GaN substrates by MOCVD on LiGaO₂ and LiAlO₂, and using the high growth rate possible with Hydride Vapor Phase Epitaxy to produce free standing GaN. Keys to obtaining high quality GaN films on LiGaO₂ are an initial surface nitridation step followed by growth of a MOCVD buffer layer. The use of hydrogen as the carrier gas and avoiding the buffer layer was possible when using LAO as a substrate. A self-separating technique was developed that leaves freestanding flat single crystal GaN without mechanical or chemical treatment. It was determined that surface nitridation and cooling process are critical to delaminating.

11:30 AM J1.7

A NOVEL SAPPHIRE SURFACE GROWTH PROCESS FOR LED SUBSTRATE APPLICATIONS. Hyoungjoon Park, Helen M. Chan, Lehigh University, Dept of Materials Science & Engineering, Bethlehem, PA.

At present, sapphire substrates for blue LED and laser diode applications are prepared by a combination of mechanical and chemical polishing. The ensuing device performance is highly dependent on the quality of the surface finish, and degree of subsurface damage. Results will be presented on a new approach to generating a pristine surface layer, starting with a sapphire substrate mechanically polished to a 3 micron diamond finish. The process consists of oxidation of a thin surface film of Al, followed by solid phase epitaxy of the underlying substrate. Development of the surface layer was studied using SEM, OIM (orientation image microscopy), X-ray diffraction, and AFM. The influence of coating temperature and heat treatment time/temperature on the final surface finish will be discussed. The proposed method has the potential to be more cost-effective than conventional techniques, and would be compatible with current device manufacturing procedures.

11:45 AM J1.8

GaN EPITAXIAL LAYERS ON SELF-FACETED SHAPED Al₂O₃:Ti⁺³ RIBBONS. V.I. Nikolaev, A.E. Nikolaev, S.I. Bacholdin, V.M. Krymov, A.F. Ioffe Physico-Technical Institute, St. Petersburg, RUSSIA; V.A. Ivantsov, TDI Inc., Gaithersburg, MD.

It looks attractive to fabricate broadly tunable laser with diode pumping where diode structures are grown directly on laser crystal. One of the most prospective materials for the application is titanium-doped sapphire. It is well known that laser generation in Al₂O₃:Ti⁺³ is available in the range 675-945 nm [1] and from the other hand sapphire is preferred substrate for the growth of GaN based LED heterostructures. There is the opinion that fitting of wavelength of the light emission maximum of the heterostructures to the peak position of the Al₂O₃:Ti⁺³ absorption spectrum by changing of In/Ga ratio in nitride composition has to provide effective pumping such device. The present work is the first step in this direction. The ribbon Al₂O₃:Ti⁺³ crystals have been produced by Stepanov's (EFG) technique from the melt using special shaper. The pull rate was typically 0.15-0.3 mm/min. The crucible charge consisted of crystal Al₂O₃ and powder of TiO₂ (0.1 percent by weight). The grown 10-mm wide ribbons were slightly crimson, self-faceted by basal plane (0001) and looked mirror like. 3-5µm-thick GaN epitaxial layers have been deposited on the as-grown surface of the ribbons without any buffer layers in hot-wall horizontal HVPE reactor operated at 900-1150°C. The investigation of PL and CL spectra of the layers and the substrates has shown that they are typical for high-quality GaN and Al₂O₃:Ti⁺³ crystals. I. G.S. Kruglik, G.A. Skripko, A.P. Shkadarevich et al. Quant. Electronics (Russian) 13, 1207 (1986).

SESSION J2: INORGANIC MATERIALS FOR SOLID-STATE LIGHTING II

Chair: Alan F. Wright
Monday Afternoon, November 26, 2001
Room 301 (Hynes)

1:30 PM *J2.1

WHITE LEDs BASED ON SEMICONDUCTORS. E. Fred Schubert, Department of Electrical and Computer Engineering, Boston University, Boston, MA.

This talk will review experimental and theoretical results on a GaInN-based LED capable of emitting white light with high efficiency. The LED consists of a current-injected blue LED and an electrically passive but optically active photon-recycling region. Several characteristics of the photon-recycling semiconductor LED, including

the luminous performance, color rendering properties, and current crowding, will be discussed.

2:00 PM *J2.2

TECHNICAL AND COMMERCIAL CHALLENGES FOR ILLUMINATION WITH BLUE/UV AND PHOSPHOR SOLID STATE LIGHTING. Robert F. Karlicek, Jr., GELcore, Valley View, OH.

It is widely recognized that the development of high brightness GaN based LEDs has created opportunities for the development of solid state lighting systems for general (white light) illumination. In order for solid state lighting to begin to penetrate the illumination market, a 5 to 10 fold performance improvement (in terms of Lm/W) as well as a 5 to 10 fold cost reduction (in terms of /kLm) will be needed. Achieving these improvements will require significant breakthroughs in LED chip performance, phosphors, power packaging and optics. This talk will review the technical and market challenges faced by LED solutions for illumination, contrast the various approaches which use LEDs to produce white light, and look at improvements in conventional lighting systems that will continue to challenge LED based solid state illumination developers in the near future.

2:30 PM J2.3

DEGRADATION STUDIES OF AlGaInP HIGH-BRIGHTNESS LIGHT EMITTING DIODES. A. Jaeger, P. Stauss, N. Linder, K. Streubel, R. Oberschmid, OSRAM Opto Semiconductors, Regensburg, GERMANY.

Visible light-emitting devices (LEDs) are of utmost importance for many applications such as automobile lighting, signs, liquid crystal display backlighting and in the near future for general lighting. Compared to conventional incandescent bulbs LEDs have several advantages including higher luminous efficiencies and higher reliability. These goals require an optimized epitaxial growth. Additionally, we utilize an improved contact geometry and a new type of surface texturing. AlGaInP LEDs with a dominant wavelength of 615 nm and different thicknesses of spacer layer between the active multiquantum well region and the p-contact layers are analyzed by both optical and electrical measurements during long-term high-brightness operation. Light-current characteristics supplemented by current-voltage characteristics reveal a strong dependence of device reliability on the layer design. LEDs with a thin spacer layer suffer from a strong increase of non-radiative recombination processes in the active layer resulting in reduced optical power during the first 100 hours. In contrast, a thick spacer layer improves considerably the reliable operation of LEDs with no changes during the first 600 hours. This result can be understood in terms of the different concentration of non-radiative defects connected to p-dopand Mg atoms in the device which can be activated during operation. In conclusion, we demonstrate analytical tools which are sensitive to gradual operation-induced changes of high-brightness LEDs and allow insights into the aging mechanisms occurring during long-term operation. Highly reliable AlGaInP LEDs are fabricated by an optimized epitaxial growth design.

2:45 PM J2.4

LOW-TEMPERATURE GROWTH OF SiCAlN FILMS OF HIGH HARDNESS ON Si(111) SUBSTRATES. Radek Roucka, Arizona State University, Department of Physics and Astronomy, Tempe, AZ; John Tolle, Arizona State University, Department of Chemistry and Biochemistry, Tempe, AZ; David J. Smith, Arizona State University, Department of Physics and Astronomy and Center of Solid State Science, Tempe, AZ; Peter Crozier, Arizona State University, Center of Solid State Science, Tempe, AZ; I.S.T. Tsong, Arizona State University, Department of Physics and Astronomy, Tempe, AZ; John Kouvetakis, Arizona State University, Department of Chemistry and Biochemistry, Tempe, AZ.

Thin films and coatings of the solid solution SiCAlN are deposited on Si(111) substrates at low temperatures using a completely new approach based upon thermally activated reactions of a unimolecular precursor H₃SiCN with Al atoms from a Knudsen cell in a molecular beam epitaxy (MBE) chamber. The reaction produces SiCAlN films accompanied by the elimination of hydrogen as a byproduct. The reaction proceeds at substrate temperatures in the range of 550-750°C, considerably lower than previous attempts in the growth of films of similar composition. Fourier transform infrared spectroscopy (FTIR) in the transmission mode shows two broad peaks at wavenumbers 737 cm⁻¹ and 660 cm⁻¹ corresponding to Si-C and Al-N lattice vibrations respectively. Elemental concentration of the films determined by Rutherford backscattering spectrometry (RBS) shows Si at 25 at.%, Al at 27-29 at.%, C at 23-24 at.%, and N at 24-26 at.%. High resolution cross-sectional transmission electron microscopy (XTEM) images of the SiCAlN films show columnar growth of wurtzite structure with lattice constants a = 3.06 Å and c = 4.95 Å determined from electron diffraction patterns, close to those of

2H-SiC and hexagonal AlN. Electron energy loss spectroscopy (EELS) with nanometer beam size yields all four elements Si, Al, C and N at every position probed, and these elements are uniformly distributed across the columnar grains in the film, indicating a solid solution of SiCAlN. Using a nano-indentor, we measure an average hardness of 25 GPa for the films, comparable to that measured for sapphire.

3:30 PM *J2.5

STACKED AlGa_N/InGa_N DOUBLE HETEROSTRUCTURES FOR MULTICOLOR AND WHITE LIGHT EMISSION. S.M. Bedair, Electrical and Computer Engineering Department, North Carolina State University, Raleigh, NC.

InGa_N ternary alloys can be the basis for light emission from the near UV to the red region of the spectrum. When InGa_N/AlGa_N double quantum well heterostructures emitting different colors are stacked in a single structure, simultaneous emission of different wavelengths can be achieved. If the color and the intensity of emission of each well are adjusted, tailored emission spectra, including white light, will be feasible. We demonstrated this concept and will report on progress toward achieving a solid-state white light bulb.

4:00 PM J2.6

ELECTROLUMINESCENT DISPLAY DEVICES ON GLASS USING A HIGH TEMPERATURE STABLE GaN-BASED PHOSPHOR AND THICK-FILM DIELECTRIC LAYER. J. Heikenfeld and A.J. Steckl, University of Cincinnati, Nanoelectronics Lab, Cincinnati, OH.

We have developed a novel display structure which has improved the brightness and large area fabrication feasibility of rare earth (RE) doped GaN display devices[1]. Through use of hexagonal GaN growth promotion on an AlN/In₂O₃:Sn/glass or ZnO:Al/glass substrates, GaN:RE EL phosphors are now compatible with the same substrates utilized in active matrix liquid crystal display manufacturing. Furthermore, screen-printing of a high-yield, high-capacitance ($\epsilon \sim 1000$) thick film dielectric layer has been used as the primary dielectric layer in an alternating current EL device. The high temperature stability of GaN:RE phosphors makes possible the fabrication of this novel thick dielectric EL (TDEL) device on glass substrates. White and primary color light emission from red (Ga_N:Eu), green (Ga_N:Er), and blue (Ga_N:Tm) TDEL devices has been developed. For biasing at 1 kHz, GaN:RE EL brightness has been improved by an order of magnitude for all thin film EL devices to ~ 40 cd/m² for TDEL devices. Furthermore, TDEL device contrast measured in 140 lux office lighting has been improved to nearly 10:1 for 120V, 1kHz biasing. The aging of GaN:RE display devices has been improved to the point where after 1000 hrs of operation only a 5% reduction in brightness is observed. GaN:RE TDEL devices provide key fabrication advantages required for display technology[2] in development for >30" diagonal HDTV. Through use of the GaN:RE phosphor, the additional advantages of reduced fabrication steps and use of standard display sheet glass are procured. The combination of these features indicate the significant potential of GaN:RE phosphors in flat panel display applications. [1] J. Heikenfeld and A.J. Steckl, Appl. Phys. Lett. 77 (22), 3520 (2000). [2] S. Grossman, Electronic Design, p. 25, May 1 (2000).

4:15 PM J2.7

RARE-EARTH DOPED STRONTIUM ALUMINATE PHOSPHORS PREPARED BY TWO DIFFERENT SOL-GEL PROCESSES. Yongxiang Li, Dong Wang, Yuhong Xiong, Yiqing Lu, Qingrui Yin, Laboratory of Functional Inorganic Materials, Shanghai Institute of Ceramics Chinese Academy of Sciences, Shanghai, CHINA.

There has been increasing interest on strontium aluminate phosphors doped with rare-earth metal ions because of their high quantum efficiency, anomalous long phosphorescence and stability. They have been widely discussed as a substitute for the conventional ZnS:Cu, Co with a radioactive material in recent years. In previous reports the solid-state reaction process has been used intensively to the synthesis of the materials, but this process results in low homogeneity, high calcinating temperature and limited applications. The sol-gel method is an emerging route with high promise for very homogeneous films, which can be formed at relatively low temperatures. In this paper, two kinds of sol-gel processes were applied to prepare SrO₂Al₂O₃:Eu, Dy phosphor powders and films. One is the aqueous sol-gel process, which uses aluminium nitrate, strontium nitrate, europium nitrate and dysprosium nitrate as starting material. The other is metal alkoxide process, which uses aluminium iso-propoxide, strontium acetate, europium nitrate, and dysprosium nitrate as starting materials and glycerol as an additive. The X-ray diffraction and fluorescence spectra were investigated to characterize the phosphors and films prepared by two sol-gel processes, and the results were compared with those of the materials synthesized by conventional solid-state reaction process.

SESSION J3: ORGANIC LIGHT-EMITTING DIODES

Chair: Mark E. Thompson
Tuesday Morning, November 27, 2001
Room 301 (Hynes)

9:00 AM *J3.1

ORGANIC ELECTROPHOSPHORESCENT WHITE LIGHT EMITTING DEVICES. S.R. Forrest, B. D'Andrade, S. Moller, Department of Electrical Engineering, Princeton University, Princeton, NJ.

There has been considerable attention directed at employing organic light emitting devices for use in such applications as liquid crystal display back lights and room lighting applications. However, the efficiency and maximum brightness of OLEDs to date has not made this a practical approach, particularly for the latter application. However, with the discovery of electrophosphorescence, OLED internal quantum efficiencies approaching 100% have been demonstrated, suggesting that white light emitting OLEDs may soon find use in a wide range of applications. In this work, we discuss several architectures for balanced, bright white light emission employing blue, green and red phosphors based on iridium metallorganic complexes. We find that white emission at external efficiencies >4% are easily achieved employing device structures which take advantage of the long diffusion lengths of triplet excitons. Further, we discuss simple light outcoupling schemes which extract at least 50% more light than that emitted from a flat glass substrate. Prospects for using electrophosphorescent OLEDs for white light emission applications are considered.

9:30 AM J3.2

HIGH TEMPERATURE MORPHOLOGICALLY STABLE Alq₃-BASED OLEDs. Mathew Mathai, Keith Higginson, Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Bing Hsieh, Canon R&D Center Americas, Inc., San Jose, CA.

Stable operating characteristics of Alq₃ based OLEDs in excess of 5000 hours of continuous operation have been achieved by means of modifying the ITO anode with a thick (2000Å) Oxidized Transport Layer (OTL). A systematic analysis of the various failure mechanisms suggest that minimizing the excess holes in the Alq₃ layer plays an important role in increasing the device longevity and fabrication simplicity. Combining this with morphological improvements employing entropic stabilization of the Alq₃ layer by means of blending with 4-methyl Alq₃ poses a viable strategy in improving stability for temperatures in excess of 90°C. In addition, the presence of OTL provides a natural way to optimize and tune device brightness at low voltage (3-5 Volts), as well as provide an intrinsic mechanism to prevent excessive current variation due to voltage fluctuations This is done by introducing a space charge regime in the current voltage characteristics of these devices.

9:45 AM J3.3

THEORETICAL STUDIES OF METAL COMPLEXES AS PHOSPHORS IN LIGHT EMITTING DIODES. P. Jeffrey Hay and Richard L. Martin, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

Heavy metal complexes are receiving increased attention as efficient phosphors in organic light emitting diodes(OLED). Electron-hole recombination can utilize phosphorescence from the lowest triplet state rather than fluorescence from the lowest singlet state to achieve higher efficiencies. Relying upon recent advances in time dependent density functional theory (TDDFT), we have studied the nature of the lowest excited states in Ir and Pt complexes with potential OLED applications. We find that the TDDFT approximation, using hybrid density functionals, provides a surprisingly quantitative reproduction of the excitation energies in these traditionally challenging organometallic systems. For a series of Ir(ppy)₂(L) complexes studied experimentally by Thompson et al. we examine the nature of the low-lying metal-to-ligand charge-transfer (MLCT) states and how they vary as a function of L. The photophysics of the lowest triplet state in the Pt(porphyrin) complex Pt(OEP) has also been investigated.

10:00 AM J3.4

EXCITATION TRANSFER PROCESSES IN A PHOSPHOR DOPED POLY (P-PHENYLENE VINYLENE) LIGHT-EMITTING DIODE. I.H. Campbell and D.L. Smith, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM; S. Tretiak and R.L. Martin, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM; C.J. Neef and J.P. Ferraris, Department of Chemistry, The University of Texas at Dallas, Richardson, TX.

We present experimental measurements and theoretical calculations of the electrical and optical properties of phosphor doped poly

(p-phenylene vinylene) light-emitting diodes to determine the excitation processes that lead to radiative recombination from the phosphor molecule. Three possible phosphor excitation processes were considered: 1) sequential electron and hole capture by the phosphor; 2) energy transfer from the polymer triplet exciton (Dexter transfer); and 3) energy transfer from the polymer singlet exciton (Forster transfer). The properties of the doped polymer were investigated for doping levels up to about 20%. At the highest doping density, all radiative recombination occurs in the phosphor molecule and the observed electroluminescence decay time increases compared to the undoped polymer. Current-voltage and built-in potential measurements indicate that the electron and hole energy levels of the phosphor are outside the energy gap of the polymer and that the phosphor molecule does not capture either individual electrons or holes. Measurements of triplet optical absorption show that the triplet population in the polymer is not affected by the presence of the phosphor indicating that Dexter transfer processes are weak. In an analogous chemically substituted polymer, no excitation transfer occurs when there is no overlap between the emission spectrum of the polymer and the absorption spectrum of the phosphor. These results demonstrate that the only active excitation transfer path from the polymer to the phosphor is dipole-dipole coupling. These conclusions are consistent with the charged and neutral electronic excitation energies of the polymer and phosphor determined by hybrid and time-dependent, density-functional-theory calculations.

10:15 AM J3.5

HIGH SPEED PULSE RESPONSE OF OLED WITH RUBRENE DOPED THIN EMISSIVE LAYER AS A LIGHT SOURCE FOR POLYMERIC OPTICAL INTEGRATION. Yutaka Ohmori, Takayuki Taneda, Takahisa Tsukagawa, Masayoshi Yamazaki and Hirotake Kajii, Osaka University, Collaborative Research Center for Advanced Science and Technology (CRCASST), Suita, Osaka, JAPAN.

Organic electroluminescent devices (OLED) have been attracted great interest for flat panel display applications. An additional advantage is that they are for simple fabrication on various kinds of substrate, including polymer substrates and have a capability of an integrated optical circuit with OLED and polymeric waveguide. In this presentation, we demonstrate the device characteristics of an OLED for the light source of polymeric waveguide. The OLED consists of an emissive layer utilizing rubrene (5,6,11,12-Tetraphenyl-naphthalene) doped in Alq3 (8-hydroxyquinoline aluminum) and a hole transporting layer of α -NPD (N,N-di(naphthalene-1-yl)-N, N-diphenylbenzidine). The device emits yellow light centered at 550 nm with 1 ~6 vol% of rubrene doped in Alq3. Since the polymeric waveguide used in our experiments have the low propagation loss at the longer wavelength side, the yellow emitting OLED with rubrene has the advantages of relatively low propagation loss and the high emission intensity. The device emits more than 30,000 cd/m² at the current density of 3 A/cm², and has a response speed of more than 30 MHz with the device of 0.1 mm²-electrode area. The OLED is directly driven at an applied voltage of 10 ~15 V, and the output light is monitored through the waveguide. The OLED with DCM (4-(dicyanomethylene)-2-methyl-6-(p-dimethyl-aminostyryl)-4H-pyran) doped in Alq3 have similar response characteristics, however, the emission intensity is stronger in rubrene doped in Alq3 than that in DCM doped device. The details of the device fabrication and their emission characteristics are discussed.

10:30 AM J3.6

OPTICAL PROPERTIES OF META-PARA POLY(PHENYLENEVINYLENES). Alexander Pogantsch, Egbert Zojer, Emil J.W. List, Technische Universität Graz, Institut fuer Festkörperphysik, Graz, AUSTRIA; Jean Luc Bredas, The University of Arizona, Department of Chemistry, Tucson, AZ and Service de Chimie des Matériaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Mons, BELGIUM; Guenther Leising, Science & Technology AT&S AG, Leoben, AUSTRIA and Institut fuer Nanostrukturierte Materialien und Photonik, Joanneum Research, AUSTRIA; Kai Mahler, Gertraude Hayn, Robert Saf, Franz Stelzer, Institut fuer Chemische Technologie Organischer Stoffe, Technische Universität Graz, Graz, AUSTRIA.

Alternating meta and para substitutions along a poly(phenylene-vinylene) (PPV) chain is a way to achieve a decreased conjugation at the meta-bonds resulting in a blue shift of the emission color compared to the exclusively para-linked polymer. Additionally one can expect to increase the quantum efficiency in these materials by inhibiting exciton migration to chemical defects acting as quenching centers. We have studied the properties of several different newly synthesized meta-para PPVs by means of UV-VIS and photoluminescence spectroscopy as well as photo-induced absorption. Electroluminescent devices possessing a blue emission color were prepared. In order to study the effect of the meta units on the conjugation in more detail the polymerization product was fractionated by GPC resulting in oligomers of different chain lengths.

We have studied photoluminescence and UV-VIS absorption in solutions and compared these results to correlated semiempirical quantum chemical calculations. We find both experimental and theoretical evidence for a different extent of conjugation over the meta bonds for the ground and the first excited state. While for the ground state a degree of conjugation is conserved resulting in a red shift of the absorption maxima with increasing chain length, the spectral positions of the vibronic peaks observed in emission are chain length independent. This behavior is attributed to the localization of the excited state on a single (three ring) para-substituted phenylene between two trans vinylene units.

10:45 AM J3.7

ON THE ROLE OF KETO DEFECTS IN THE DEGRADATION PROCESS OF POLYFLUORENE TYPE MATERIALS.

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We present spectroscopic evidence for the formation of keto defect sites in 9-monoalkylated polyfluorenes (mono-PF) which are identified as the source of a strong low energy emission band at 2.3 eV = 520 nm. This observation, which has been found in polyfluorenes and ladder type poly(para-phenylene) in photoluminescence (PL) and electroluminescence (EL) emission spectra, makes the often favored interpretation of this low energy emission band, with an ongoing aggregation or excimer formation questionable. Using UV-VIS, photoluminescence emission and infrared spectroscopy we have identified the keto defects in mono-PF acting as low energetic trapping sites for singlet excitons, which are populated by an excitation energy transfer from the polyfluorene. Moreover we find a much stronger contribution from the keto emission in EL than in PL, which is attributed to charge carrier trapping at the keto site and subsequent EL in addition to excitation energy transfer of singlet excitons from the polyfluorene to the keto site. Note that 9-bisalkylated polyfluorene which has been characterized for comparison did not show any keto defects in its pristine form. The keto defects can hence be generated directly during polymer synthesis as show for the mono-PF or can be formed as main channel of an (photo- or electro-) oxidative degradation process. The presented novel results therefore strongly indicate the key role of keto defects in the degradation effects of PF type materials and PF containing polymer light emitting devices.

11:00 AM J3.8

PHOTOPHYSICAL PROPERTIES OF DENDRONIC POLY-FLUORENES AND THEIR APPLICATION IN LIGHT EMITTING DIODES. Alexander Pogantsch, Franz P. Wenzl, Emil J.W. List, Technische Universität Graz, Institut fuer Festkörperphysik, Graz, AUSTRIA; Sepas Setayesh, Andrew C. Grimsdale, Heinz G. Nothofer, Klaus Müllen, Max-Planck-Institute for Polymer Research, Mainz, GERMANY; Guenther Leising, Science & Technology AT&S AG, Leoben, AUSTRIA.

Shielding a polyfluorene backbone with oligophenylene (Muellen-type) dendrons is a promising way to reduce interchain interactions that usually destructively influence the emission properties of the material, while retaining good charge transport capabilities. We have characterized the material using UV-VIS and photoluminescence emission spectroscopy. Upon photoexcitation only emission from the polyfluorene backbone is detectable. We have found no additional emission bands neither at lower energies nor from the dendronic side chains. Utilizing time resolved fluorescence spectroscopy we present evidence that the interchain migration of excitons is reduced in dendron-shielded polyfluorenes compared to non-shielded ones. Photoinduced absorption measurements reveal low triplet and polaron formation ratios upon photoexcitation and an excited state absorption that is spectrally well separated from the emission of the material. Using the material as the active layer in polymer light emitting devices results in stable deep blue emission with onset voltages of about 6V and a luminance of 400cd/m² at 8V. Operating the device under pulsed excitation results in a shift of the recombination zone further improving the emission color by influencing the self absorption conditions.