Tuesday Morning, October 3, 2000

Flat Panel Displays Room 313 - Session FP-TuM

Luminescent Materials

Moderator: B.E. Gnade, University of North Texas

8:20am FP-TuM1 Cross-sectional TEM Investigation of the Dead Layer of ZnS:Ag,Al Phosphors in Field Emission Displays, *K. Kajiwara*, Sony Corporation, Japan

The dead surface layer of blue-emitting ZnS:Ag,Al phosphor was investigated by means of cross-sectional transmission electron microscopy for the first time. It was found that the electron radiation-induced damage at 6 keV excitation gives rise to (i) the decomposition of ZnS and the evolution of sulfur at the topmost surface, and (ii) the nucleation and multiplication of lattice defects, for example vacancy clusters and dislocations, at the electron penetration layer of approximately 300 nm. It was estimated that the decompositon rate of ZnS and the nucleation rate of defects depend on the crystallinity and surface roughness of the ZnS host crystal. Based on these evidences, necessary specifications of ZnS:Ag,Al phosphor for the long lifetime of field emission display are to be discussed in this preliminary work.

8:40am FP-TuM2 Enhanced Activator Interactions During Low Electron Energy Cathodoluminescence, C.H. Seager, D.R. Tallant, Sandia National Laboratories INVITED

We have measured the time decay of spectrally-resolved, pulsed cathodoluminescence (CL) and photoluminescence (PL) in several phosphors activated by rare earth and transition metal impurities; These included Y@sub 2@O@sub 3@:Eu, Y@sub 2@SiO@sub 5@:Tb, and Zn@sub 2@SiO@sub 4@:Mn; typical activator concentrations ranged from ~ 0.25 to 10%. The CL decay curves are always non-linear on a log-linear plot - i.e. they deviate from first order decay kinetics. These deviations are always more pronounced at short times and larger activator concentrations and are largest at low beam energies where the decay rates are noticeably faster. PL decay is always slower than that seen for CL, but these differences disappear after most of the excited species have decayed. We have also measured the dependence of steady state CL efficiency on beam energy. We find that larger activator concentrations accelerate the drop in CL efficiency seen at low beam energies. These effects are largest for the activators which interact more strongly with the host lattice. While activator-activator interactions are known to limit PL and CL efficiency in most phosphors, the present data suggest that a more insidious version of this mechanism is partly responsible for poor CL efficiency at low beam energies. This "enhanced" concentration quenching is due to the interaction of nearby excited activators; these interactions can lead to nonradiative activator decay, hence lower steady state CL efficiency. Excited state "clustering" appears to enhance these interactions, and this may be caused by the large energy loss rate of low energy primary electrons. In support of this idea, we find that PL decays obtained at high laser pulse energies replicate the non-linear decays seen in the CL data. This work was supported by DARPA. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract #DE-AC04-94AI 85000

9:20am FP-TuM4 Growth and Characterization of Pulsed Laser Deposited Zn2GeO4:Mn Green Thin Film Phosphors, T. Feng, P.H. Holloway, D. Kumar, M. Davidson, University of Florida; J.M. Fitz-Gerald, H. Kim, Naval Research Laboratory; D.P. Norton, Y.E. Lee, Oak Ridge National Laboratory Pulsed laser deposition of Zn2GeO4:Mn oxide thin films on glass/ITO/ATO and Al2O3/Au/PZT substrates, which are potentially used for electroluminescent displays, has been investigated. A stoichiometric target Zn2GeO4:Mn was obtained by sintering a mixture of ZnO, GeO2 and MnO2 powder in air at 1020oC for 24 hrs. A green photoluminescence peak was obtained from the target at a wavelength of 540nm. Films were pulsed laser deposited on glass/ITO/ATO and Al2O3/Au/PZT substrate at an O2 pressure of 150~200 mTorr and a laser density of 0.8~1.6J/cm2. All deposited films were Zn-deficient in contrast to the stoichiometric target ratio for Zn/Ge of 2. The films deposited at 250oC on glass/ITO/ATO showed a Zn/Ge ratio of 1.02, while films deposited at 800oC were more Zn-deficient with a ratio of 0.82. The Zn2GeO4:Mn films deposited at 250oC on glass/ITO/ATO were amorphous, but recrystallized upon rapid thermal annealing at 800oC in Ar for 1 min. Photoluminescence with an intensity of 46 cd/m2 at a peak wavelength of 536nm was obtained from a

300nm film deposited on Al2O3/Au/PZT at 250oC followed by postannealing at 750oC in air for 1 hr. Photoluminescence of 11 cd/m2 was obtained from a film deposited on glass/ITO/ATO followed by rapid thermal annealing at 800oC in Ar for 1 min. A surface particulate density of 2.42x105/cm2 was observed in the film deposited on glass/ITO/ATO substrate at a temperature of 250oC, O2 ambient pressure of 200 mTorr and laser density of 0.8mJ/cm2. Films deposited at 800oC showed a large density of pinholes, in addition to surface particulates. Annealing in O2 ambient resulted in a better PL intensity compared to annealing in air or Ar ambient.

9:40am FP-TuM5 Energy Loss Mechanisms in Pulsed Laser Coated Cathodoluminescent Phosphors, W.J. Thomes, P.H. Holloway, University of Florida; C.H. Seager, D.R. Tallant, Sandia National Laboratories

Coatings of MgO and Al@sub 2@O@sub 3@ were pulsed laser deposited onto sedimented screens of Y@sub2@O@sub 3@:Eu and Y@sub 2@SiO@sub 5@:Tb to study energy loss mechanisms in the coatings and to predict their impact on cathodoluminescence (CL). The thickness of the pulsed laser deposited coatings, characterized by ellipsometry, TEM and AES sputter profiles, were varied from 75 to 500 Angstroms by changing the deposition time and oxygen background pressure. A Si shadow mask covered half of the sedimented powder during deposition to allow comparison of coated and uncoated powder. DC and pulsed cathodoluminescence data were collected using an Ocean Optics fiber optic spectrometer or a modified Kimball Physics electron gun, respectively. Light was collected using fiber optics connected to a photomultiplier tube or a CCD detector. The beam energies were varied from 0.8 to 4 keV, while the current was kept constant at 0.16 μ A/cm@super 2@. The coating thickness on particles was modeled by assuming a uniform flux depositing over a spherical powder surface. Spatially resolved electron energy loss was calculated to predict the CL intensity versus beam energy and incident angle relative to the local surface normal. The predictions of the CL intensity versus incidence angle, coating thickness, and primary beam energy agreed well with experimental data. The consequences of these data relative to phosphor degradation and low voltage efficiency will be discussed.

10:00am FP-TuM6 Effect of He/Ar Sputtering Gas Mixture on the Brightness of RF Magnetron-Sputtered ZnS:TbOF for Alternating Current Electroluminescent Displays, J.P. Kim, M. Davidson, D. Moorehead, P.H. Holloway, University of Florida

ZnS:TbOF has shown promise as a green electroluminescent phosphor. We have studied the effects of He/Ar mixture as ambient gas on the brightness of ZnS:TbOF thin film electroluminescent devices. ZnS:TbOF phosphor films were planar magnetron sputter deposited from consolidated powder targets of ZnS:TbOF (1.5 mol %) at 120W. All films were deposited at a substrate temperature of 160°C and total pressure of He/Ar gas was kept at 20mTorr. Helium gas ratio was changed from 0% to 70%. Top insulator layer was planar magnetron sputter deposited from consolidated powder targets of BaTa@sub 2@O@sub 6@. The sputtering deposition rate of ZnS:TbOF was in the range of 84Å/min - 113Å/min and was not changed significantly by increasing the He/Ar ratio. He/Ar gas mixture up to 50% He don't result in any significant change of the brightness (B@sub 40@@super half@) of half stack structures (bottom dielectric layer and top Al dot contact directly on the ZnS:TbOF) for either as-deposited or annealed films (500 °C,60 min). At a higher helium ratio (> 60%), the B@sub 40@@super half@ decreased for both as-deposited and annealed films (500 °C, 60 min). Surface roughness was less for >60% He, as measured by Atomic Force Microscopy (AFM). Full Width of Half Maximum (FWHM) from X-ray diffraction showed increased crystallinity of deposited film > 60% He. Films deposited at > 60% He exhibited higher dielectric constants. Therefore, the brightness decrease in high helium is attributed to reduced roughness and increased dielectric constant of the phosphor layer. This work was supported by DARPA Grant MDA 972-932-1-0030 through the Phosphor Technology Center of Excellence.

10:20am FP-TuM7 Eu@super +3@ and Cr@super +3@ Doping for Red Cathodoluminescence in ZnGa@sub 2@O@sub 4@, J.J. Peterson, Advanced Vision Technologies, Inc.; P.D. Rack, Rochester Institute of Technology; M.D. Potter, Advanced Vision Technologies, Inc.

Cathodoluminescence (CL) emission spectra and photoluminescence (PL) excitation spectra were used to evaluate Eu@super +3@ and Cr@super +3@ as activators for red luminescence in ZnGa@sub 2@O@sub 4@. In the Eu@super +3@ doped ZnGa@sub 2@O@sub 4@ materials blue host emission was observed at high current densities and is attributed to ground state depletion of the Eu@super +3@ activators. In addition, PL excitation

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measurements revealed poor energy-transfer from the ZnGa@sub 2@O@sub 4@ host to the Eu@super +3@ ions. Cr-doping resulted in a saturated red-color and no host emission was observed over the entire current density regime investigated. The PL excitation of the ZnGa@sub 2@O@sub 4@:Cr@super +3@ revealed good overlap between the host emission and the O-Cr@super +3@ ligand-to-metal charge transfer absorption band. Cathodoluminescence efficiency and emission spectra of various compositions will be presented as a function of current density. The relevant energy transfer theory for the red emission in Eu@super +3@ and Cr@super +3@ doped ZnGa@sub 2@O@sub 4@ will be discussed. Finally, a process that integrates Cr@super +3@ (red), Mn@super +2@ (green) and intrinsic ZnGa@sub 2@O@sub 4@ (blue) into a single thin film for high-resolution field emission display applications will be shown.

10:40am FP-TuM8 Molecular Organic Light-Emitting Devices based on a Guest-Host System, Z.H. Kafafi, H. Murata, L.C. Picciolo, Naval Research Laboratory INVITED

This talk will review the molecular and electronic properties of the guests and hosts used in the active emissive layers in molecular organic lightemitting devices (MOLEDs), and the electrical and luminescent characteristics of MOLEDs with high efficiency, good thermal stability and extended lifetime. Saturated red, green and blue (RGB) emission based on a common host will be discussed in terms of energy transfer from the host to the guest molecules, and direct electron-hole recombination on the highly luminescent guest molecules. The mechanisms leading to high electroluminescence quantum efficiency and, good thermal and temporal stability will be discussed.

11:20am FP-TuM10 Aging and Luminescent Characterization of Coated ZnS:Ag Phosphors in FED Systems, G.R. Villalobos, J.S. Sanghera, I. Aggarwal, Naval Research Laboratory

Sulfide phosphors used in field emission displays (FED) tend to degrade (both physical and luminescent degradation) from interaction with the emitted electrons and residual gases in the device vacuum. A variety of coating types may protect the phosphors from degradation. For example, inert buffer coatings can isolate the phosphor from the residual gases in the device vacuum, electrically conductive coatings can reduce the surface charging, and thermally conductive coatings could reduce the heating from the electron beam on the phosphor surface. It is also possible that a layered structure composed of these individual coatings could be of benefit. We have scaled up a process that we developed to hermetically coat individual phosphor particles with various films. Whereas the laboratory-sized process could coat a half-gram of phosphor per day, the pilot plant scale system can coat up to 100 grams per day without a reduction in luminescent properties. To date we have deposited SiO@sub 2@, MgO, ITO, and Na(PO@sub 3@)@sub 6@ coatings on ZnS:Ag phosphors. The process allows a precise control over the thickness of the coating. Coating thicknesses of 5 to 90nm have been achieved. The process is continuous, is fully automated, and further scaleable to industrial sizes. The cathodoluminescent (CL) efficiency and aging behavior of the SiO@sub 2@ coated phosphor has been measured in both laboratory and FED devices. Aging tests have shown a dramatic improvement in aging behavior between the coated and un-coated phosphors. While phosphor efficiency and chromaticity are within 10% of uncoated values. Future work will include the measurement of the other coating materials.

11:40am FP-TuM11 Temperature Dependence of Cathodoluminescent Degradation of ZnS Phosphor, *B. Abrams*, University of Florida; *W. Roos*, University of the Orange Free State; *L.C. Williams*, *P.H. Holloway*, University of Florida

The effect of temperature on ZnS:Ag,Cl cathodoluminescent (CL) intensity and degradation by surface chemistry changes has been investigated using an Oriel optical spectrometer and a scanning Auger electron spectrometer. With vacuum pressures maintained between 3-5x10@super-9@ Torr, thermal quenching has been measured on the ZnS:Ag,Cl powder pressed into an Al cup and mounted onto a heater stage. Using a 2kV accelerating voltage, a constant current of 5µA and a 1mm spot size, the sample temperature was incrementally increased to 400@supero@C with CL and AES measurements being taken after each increase. AES data show little change in the S. Zn. O and C peaks on the surface as the temperature is increased. There is also no significant shift in Auger peak energies with temperature. The CL brightness decreased dramatically at T@>=@300@supero@C, while the maximum CL peak intensity shifted from 450nm to almost 600nm. CL brightness measurements taken as the sample was incrementally cooled back towards room temperature showed that the most intense CL peak shifted back to 450nm. However, a large

hysteresis was observed in the CL intensity versus temperature data due to poor heat transfer. Recovery of the CL intensity upon returning to RT ranged from 70% recovery to 100% recovery dependent upon the hold time at each temperature. The mechanisms for these effects will be discussed. This work was supported by DARPA Grant MDA 972-93-1-0030 through the Phosphor Technology Center of Excellence.

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