About the 1996 Electronic Materials Conference: Wednesday Afternoon Sessions (June 26)

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Session H: Organic Light Emitting Devices

Session Chairman: Ron Moon, Hewlett Packard Laboratories, Solid State Technology Lab., 3500 Deer Creek Road, Palo Alto, CA 94304. Co-Chairman: Yang Yang, UNIAX Corp., 6780 Cortona Drive, Santa Barbara, CA 93117

1:30PM, H1 *Invited

"Light Emitting Devices Based on Organic Thin Film Heterostructures:" M.F. RUBNER, Department of Materials Science and Engineering, MIT, 77 Massachusetts Avenue, Cambridge, MA 02139

New light emitting multilayer heterostructures have been fabricated from a variety of different materials including conjugated polymers, ruthenium complexes and organic luminescent dyes. Light emitting devices with high luminance levels (in some cases > 2000 cd/m^2) and tunable emission wavelengths have been created through the use of multi-bilayer "slab" systems that are used to control the charge injection and transport characteristics of the device. Molecular level processing schemes have been used to manipulate the nature of the thin film/electrode interfaces present in these devices. For example, the addition of a 3 mm thick insulating layer at the PPV/aluminum interface of self-assembled PPV thin films has been found to improve device efficiency by a s much as a factor of five. Light emitting devices based on new processible ruthenium complexes have been found to exhibit high luminance levels and good device stability. Details concerning the behavior of these new devices and the mechanisms of charge injection and transport operating in these new multilayer thin films will be discussed.

2:10PM, H2

"Improved Brightness and Lifetime of MEH-PPV Light-Emitting Diodes Using Polyaniline Anodes:" SIEGFRIED KARG, J. Campbell Scott, IBM Research Division, IBM Almaden Research Center, 650 Harry Rd., San Jose, CA 95120-6099; Marie Angelopoulos, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY 10598

We describe a device model for organic light emitting diodes. The model uses drift-diffusion equations for electron-and hole-like excitations, coupled through Polsson's equation. In the model charge injection at the metal/organic contacts occurs by two mechanisms: thermionic emission and tunneling. Thermionic emission is dominant at low bias and tunneling is dominant at the higher bias typical of actual device operation. We first consider single carrier devices (say holes) in which the Schottky barrier for one of the two carrier types (electrons in this case) is too large to allow efficient charge injection of that carrier type. We find that because of the low mobilities typical of organic materials, there is substantial back flow of injected charge back into the injecting contact. The back flow current is proportional to the hole density near the hole injecting contact. This hole density is determined by the condition that the tunneling and back flow currents nearly cancel. The net device current is determined primarily by drift of this hole density which, because of the small mobility, is much smaller than the tunneling or back flow currents. This result explains the experimental observation that measured devices currents satisfy the Fowler-Nordheim tunneling functional dependence on electric field but are

Luminances comparable to TV screens (~100 cd/m^2) can be obtained routinely at drive voltages below 3V, and luminances exceeding those of florescent tubes at ~5V. External quantum efficiencies up to ~2.5% have been demonstrated for orange LEDs and ~2.0% for blue LEDs. Power efficiencies in excess of 4 lm/W have been demonstrated at 620nm. The use of Polyaniline has proven to be an important electrode material. Lifetimes under stress at high brightness (~100cd/m^2) will be discussed. Large area LEDs (> 25 cm^2) have been fabricated. Flexible LEDs, based on mylar substrates have also been demonstrated. The development of a wide range of new electroluminescent polymers has opened up the full color spectrum (including white). Arrays of pixels can easily be fabricated from polymers LEDs. Prototype 7-segment and 5x7 displays have been fabricated and will be discussed.

3:30PM, H5 *Invited

"Polymer LEDs - Device Performance and Applications:" I.D. PARKER, Y. Yang, G. Yu, C. Zhang, Q. Pei, E. Baggao, A.J. Heeger, UNIAX Corporation, 6780 Cortona Dr., Santa Barbara, CA 93117

We demonstrate tuning of metal-organic Schottky barrier heights in organic electronic devices by utilizing chemically tailored electrodes. The Schottky barrier height was controlled by using self-assembled monolayers (SAMs) to attach well defined dipole layers to metal contacts prior to device fabrication. SAMs with dipole moments directed away from the metal substrate (electric field pointing toward the substrate) were used to decrease the electron Schottky barrier by up to 0.7 eV in organic diode test structures. Similarly, a SAM with a dipole moment directed toward the substrate increased the electron Schottky barrier (decreased the hole Schottky barrier) by 0.5 eV.

The structure and coverage of the monolayers was assessed using infrared absorption and contact angle measurements. The change in surface potential of the metal films due to the dipole layers was measured using the Kelvin probe technique. The dipole moments of the SAMs, calculated using *ab initio* Hartree-Fock, are in good agreement with the surface potential measurements. The metal-organic Schottky barrier height in the organic diode test structures was measured using an electroabsorption technique. The effect of the dipole layer on the Schottky barrier height is consistent with the ideal Schottky model.

4:10PM, H6

"Controlling Schottky Barrier Heights in Organic Electronic Devices Using Chemically Tailored Electrodes:" I.H. CAMPBELL, S. Rubin, T.A. Zawodzinski, J.D. Kress, R.L. Martin, D.L. Smith, MS D429, Los Alamos National Laboratory, Los Alamos, NM 87545; J.P. Ferraris, The University of Texas at Dallas, Department of Chemical Engineering, Box 688, Richardson, TX 75083

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4:30PM, H7+

"Strong Electroluminescence from Molecularly Doped Polymers:" C.C. WU, J.C. Sturm, R.A. Register, *M.E. Thompson, Advanced Technology Center for Photonic and Optoelectronic Materials, Princeton University, Princeton, NJ 08544; *Chemistry Department, University of Southern California, Los Angeles, CA 90089

In this paper, we report LED's made from a new family of molecularly doped polymers (MDP), in which the hole-transporting matrix polymer poly(9-vinylcarbazole) (PVK) is doped with the electron-transporting molecule Tris(8-hydroxy quinolate) aluminum (Alq) and different fluorescent dyes. These devices have the advantage that they can be fabricated in a single spin-coating deposition step, without the solvent problems of separate carrier transport and emissive layers.

With the simplest ITO/spin-coated single-layer MDP/Mg:Ag structure, all these LED's show rectified I-V characteristics and emit light only under forward bias. The LED's made from PVK/Alq emit green light from the Alq doped into the polymer, but the efficiency is low, at most about 0.1%. Further doping PVK/Alq with a tiny amount of organic dyes, usually less than 1 wt% in total, transforms the luminescence spectra to those of organic dyes and dramatically raises the quantum efficiency. By tailoring the ratio between PVK, Alq and organic dyes, we have been able to achieve relatively high external quantum efficiencies, for example, 0.7% for orange-red and 0.5% for green, measuring only the light emission through the back of the glass substrate. A typical composition by weight is 100:40:X (PVK:Alq:dye, $0.1<X<1$). The organic dyes used include nile red (orange-red) and coumarin 6 (green). Practical brightness' can be obtained at reasonable operation voltage, for example, 100 cd/m^2 at about 12V and brightness ~4000 cd/m^2 at about 20V. Initial non-optimized reliability tests of devices not sealed in hermetic packages indicate that these devices can be continuously operated well over 100 hours before the brightness drops to one half of its initial value.

The small amount of organic dyes doped into the PVK/Alq are thought to function as efficient emission centers. Comparing the energy levels of PVK, Alq and organic dyes suggests of at least two possible mechanisms for the emission from these centers, i.e. the carrier trapping model and the energy transfer model. In the first case, they trap both holes and electrons and form excitons on themselves. In the latter case, they trap excitons formed on Alq. In any case, these dilutely dispersed dyes have a lower nonradiative rate of exciton recombination than the PVK/Alq matrix, and therefore lead to a much higher luminescence efficiency.

4:50PM, H8

"Degradation of Organic Electroluminescent Devices as a Function of Water and Oxygen Exposure and Temperature:" MARK HUESCHEN, Homer Antoniadas, Daniel Roitman, Jim Sheats, Jon McElvain*, Jeff Miller, Ron Moon, Hewlett-Packard Laboratories, Solid State Technology Laboratory, 3500 Deer Creek Rd., Palo Alto, CA 94304

Organic electroluminescent devices have demonstrated efficiencies, brightnesses, and operating voltages which are adequate for a number of applications. Their operating lifetimes, however, have been one barrier to application. We report an investigation of the effect on operating lifetime of the ambient gas composition and the device temperature.

The devices investigated have been primarily ITO/TPD/Alq3/Mg structures which have been made by sequential evaporation of the hole transport layer (TPD), the emitting layer (Alq3), and the cathode (Mg) onto an ITO-coated glass substrate. In some devices the Alq3 is doped with an emitting dye. The applied voltage and light output have been monitored while the devices are under constant current stress. Images of the devices under stress can be captured with a CCD camera, which allows the separation of homogenious wearout from inhomogeneous effects such as the formation of dark spots. The temperature of the devices can be controlled, and the box in which they are enclosed can be purged with any desired gas or gas mixture. Devices have been operated in dry nitrogen, humid nitrogen, and mixtures of nitrogen and oxygen. The types of degradation that have been studied are: an increase in operating voltage, a decrease in quantum efficiency, the formation of dark spots, and the formation of electrical shorts. A portion of the voltage increase will "recover" after the electrical stress is stopped, and may be due to the motion of ions through the device. The thermal activation of the

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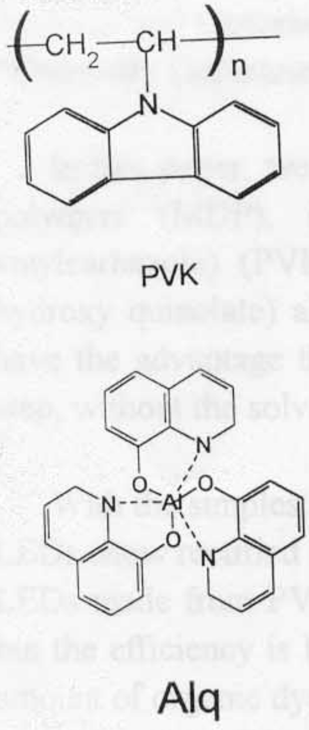

Fig. 1 Chemical structure of PVK and Alq

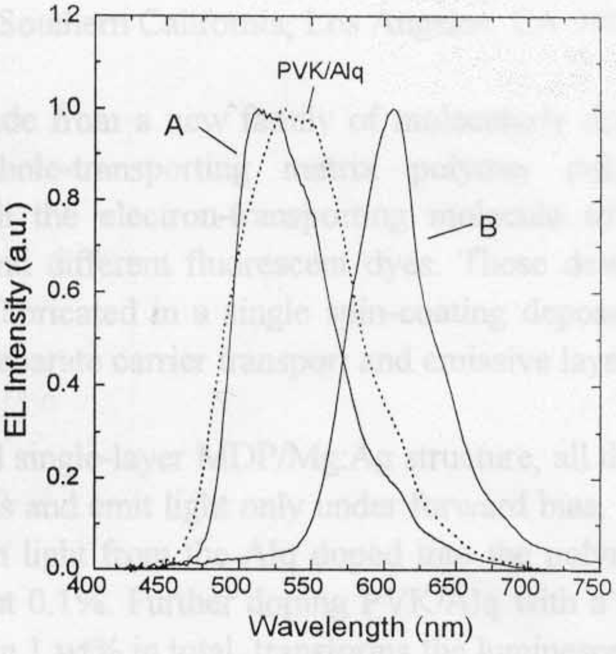

Fig. 2 Electroluminescence spectra of PVK/Alq, PVK/Alq doped with a green dye (coumarin 6, A) and PVK/Alq doped with a orange-red dye (nile red, B).

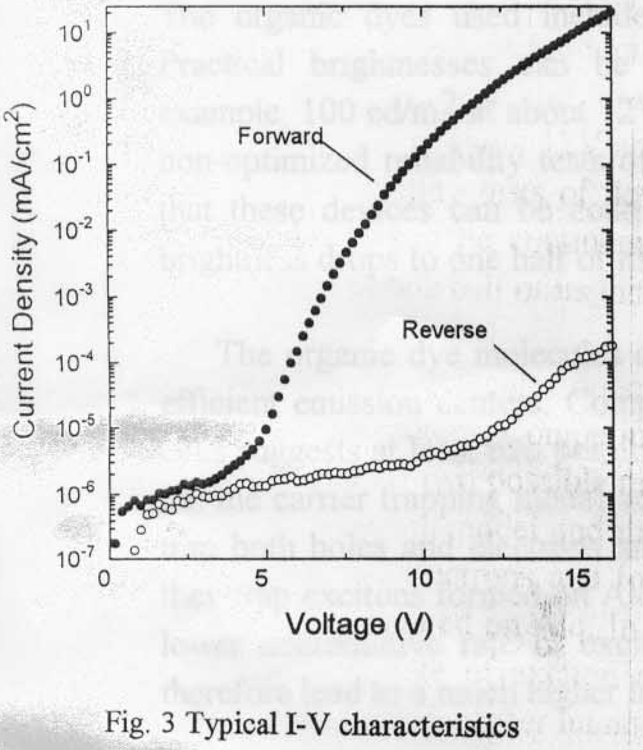

Fig. 3 Typical I-V characteristics

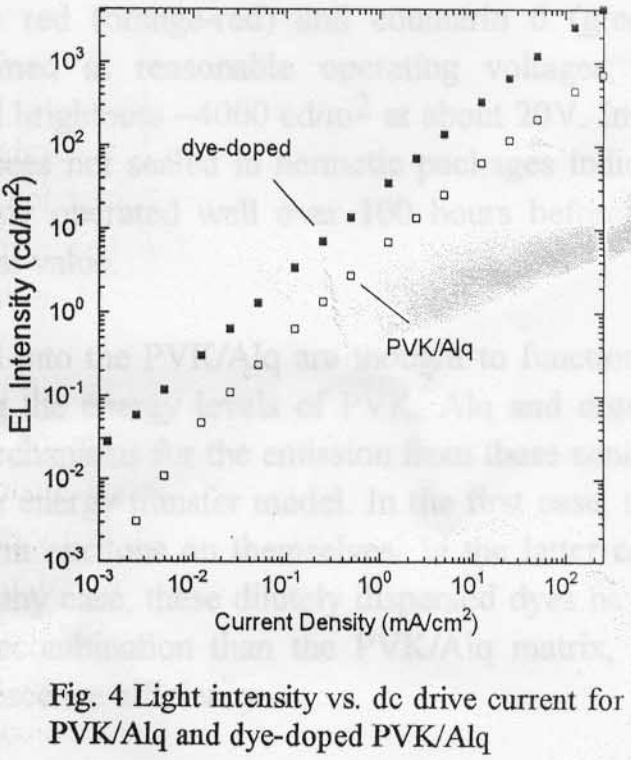

Fig. 4 Light intensity vs. dc drive current for PVK/Alq and dye-doped PVK/Alq