Acc. Chem. Res. **1999,** *32,* 193−200

ARTICLES

Chemical Aspects of Polymeric Electroluminescent Devices

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Received July 15, 1998

Introduction

Electroluminescence (EL) from organic materials was first observed in the early 1960s, during what might be considered a “golden age” of the physical chemistry of organic materials: the foundations of our current knowledge of electronic excitations, energy transport, and photochemistry were all laid in that era.[1,2] The potential of these materials for commercial application was quickly recognized, and a great deal of work has been expended over the years in attempts to develop such products as solar cells, photochromic or holographic memories, nonlinear optical devices, displays, and transistors. Until recently, however, the only significant success story was in xerography: essentially all photocopiers today use organic photoconductors.[3]

Today a second contender has finally entered the arena: Pioneer Electronics now markets a 64 × 256 pixel organic EL (OEL) monochrome display for automobiles. Although they are first to market with a product, other companies are in close contention: Philips and Uniax have both built production facilities and are prepared to supply prototype samples of OEL displays, and the list of companies and universities with R&D activity in the field runs into the dozens. One of the most dramatic announcements has been that from Cambridge Display Technology (CDT), who in an alliance with Seiko-Epson has made a 1.5 in. square, 2 mm thick, 800 × 240 pixel video screen using CDT’s EL polymer and Seiko-Epson’s polysilicon thin film transistors for active-matrix drivers.

Organic EL is obtained by placing a charge-transporting and light-emitting organic material between two electrodes (one of which is transparent) and applying a suitable bias (usually close to 1 MV/cm). Charge is injected into the HOMO at the anode (positive), and the LUMO at the cathode (negative), and these injected charges migrate in the applied field until they annihilate and produce a radiative state. The EL efficiency is primarily affected by two quantities: the photoluminescence (PL) quantum efficiency and the degree of balance of charge injection from the two electrodes. The best single-layer polymer devices have demonstrated quantum efficiencies of around 4% internally (since the light moves from a region of high refractive index into air, around 80% of it is trapped by total internal reflection in the glass substrate and waveguided out to the edges; hence, external quantum efficiency, which is the quantity of practical interest, is much lower than internal quantum efficiency). By using two organic layers, having an interface with energy level offsets, the majority charge carriers can be slowed and prevented from flowing through the device without recombination, thus increasing quantum efficiency at the expense of higher bias.

The appearance of organic electroluminescence as a practical display technology traces its origins to Tang and VanSlyke,[4] who introduced the double-layer concept in 1987: this was the first publication that combined modern thin film deposition techniques with suitable materials and structure to give a moderately low bias voltage, attractive efficiency, and encouraging lifetimes. Their devices were made by subliming molecules of a triarylamine as hole transporter, followed by aluminatotris(8-hydroxyquinolate) (Alq_3) for electron injection and emission, and a magnesium−silver alloy cathode. In 1991 Burroughes et al.,[5] at Cambridge University, reported a similar single-layer device made with a polymeric me-

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10.1021/ar980061q CCC: $18.00

dium: poly(phenylenevinylene) (PPV). The physics of charge transport and light emission in these devices is very similar; however, significant practical differences arise when one begins to contemplate manufacturing issues.

As solid-state devices, organic EL devices are often discussed using terminology drawn from traditional semiconductor physics, in which charge carriers (electrons or holes) are viewed as moving in conduction and valence bands, even though it is generally recognized that even highly conjugated polymers do not behave as fully delocalized one-dimensional solids due to the inevitable conformational defects described by the persistence length. An alternative point of view regards the relevant structural entities as radical cations and anions, and charge motion is through electron exchange reactions. The group led by Bredás (who has also contributed to this special issue) has now done calculations[6] showing rather clearly the extent of delocalization in a PPV molecule to be no more than a few repeat units, in agreement with inferences based on absorption spectra[7] and electroabsorption.[8] We believe the molecular viewpoint to be most appropriate, while recognizing that delocalization plays an important role.

Several reviews have been published to which the reader should refer for more details.[9,10] Tbe best general discussion of physical aspects is still the monograph of Greenham and Friend.[11] A concise introduction and review for a general scientific audience by the present authors and co-workers can be found in ref 1, and the relevant synthetic chemistry has been extensively described by Holmes and co-workers.[12] This Account focuses on selected aspects of device operation from a chemical perspective. In particular we address the following question: How do chemical changes affect *charge injection*, *emission efficiency*, and *operating lifetime*? Several other contributions to this issue examine such issues as charge injection and surface structure from a more physical viewpoint (in particular those by Gao, Hadziouannou, and Salaneck).

Charge Injection

Cathode. The mechanism of charge injection into polymer LED devices was first addressed by Parker,[13] who assembled an impressive set of evidence that suggested tunneling of holes and electrons into valence and conduction bands of the polymer, respectively. In this analysis, the metal work functions were taken to have their handbook values (i.e., measured on pristine surfaces), and the search for cathodes has focused on low work function metals such as calcium.

However, the reactivity of Ca with conjugated polymers was observed several years ago, primarily by XPS analysis, by research groups led by Salaneck[14] and Gao.[15] Bröms et al.[16] in fact found that some oxidation of the Ca electrode (by, for example, carrying out the deposition at a pressure of ca. 10^{-6} Torr) was necessary to obtain any working devices: ultrahigh vacuum deposition gave a zero yield.

Theoretical modeling of charge injection has been attempted by several approaches.[17−19] Excellent quantitative results have been obtained by Davids and Smith,[20] who assume injection to be a combination of thermionic emission and tunneling, but with the important feature of a thermionic backflow: if the mobility of carriers in the organic layer is small, the local concentration quickly increases and the probability of reverse hops increases. In this model, which has given good agreement with experiment for single-layer devices with both unipolar and bipolar structure, the barrier height derived from modeling is not, in general, what would be calculated from tabulated work functions.

Recently Bharathan and Yang showed[21] that just 2 Å of Ca followed by Al gives identical electrical characteristics to 2000 Å of Ca. Their data are difficult to reconcile with any mechanism other than "doping" of the interface by reaction of Ca with the polymer, creating surface states that pin the surface energy levels in a manner somewhat analogous to the pinning of the Fermi level by surface states of an inorganic semiconductor.

Even before the XPS data on alkaline earth metal reactivity had been published, it was our view as chemists that such reaction was inevitable, and the question naturally arose whether this was desirable or not. To address it experimentally, one would like to have a metal with a low work function that is impervious to oxidation. Since the former parameter is a thermodynamic one and the latter a kinetic quantity, such a combination did not seem impossible, and indeed was located in the form of certain transition metal carbides, primarily ZrC, TaC, and HfC.[22] ZrC was the easiest of these to work with, and in collaboration with William Mackie at Linfield College, thin films were prepared on sapphire substrates.

The ZrC thin films had work functions (measured by a field emission retarding potential technique) that were similar to those of bulk single crystals: about 3.6 eV. The resistivity was also similar to that of bulk: a few hundred Ω/sq.[23] The work function was not changed by exposing the film to air and reintroducing it to the UHV chamber. The resistance of a very thin film (∼100 Å) was monitored in air over a period of a few weeks, and found to rise by no more than a few percent (and to saturate after a few hours), indicating that any nonconducting interface must be at most a few angstroms thick.

Scanning tunneling microscopy (STM) observations gave a similar picture. A standard, electrochemically etched Pt/Ir tip was used to image both a single crystal and a film (both of which had been exposed to air for weeks). In both cases, images characteristic of a somewhat "dirty" conducting surface were obtained: the features were reproduced on repeated scanning, albeit with considerable noise. Typical conditions were about 600−1000 mV bias and 200−300 pA current. The topography of the crystal (evident even in an optical microscope) was clearly seen. The tip was not "crashed" nor even significantly damaged by prolonged scanning of the ZrC surface: after

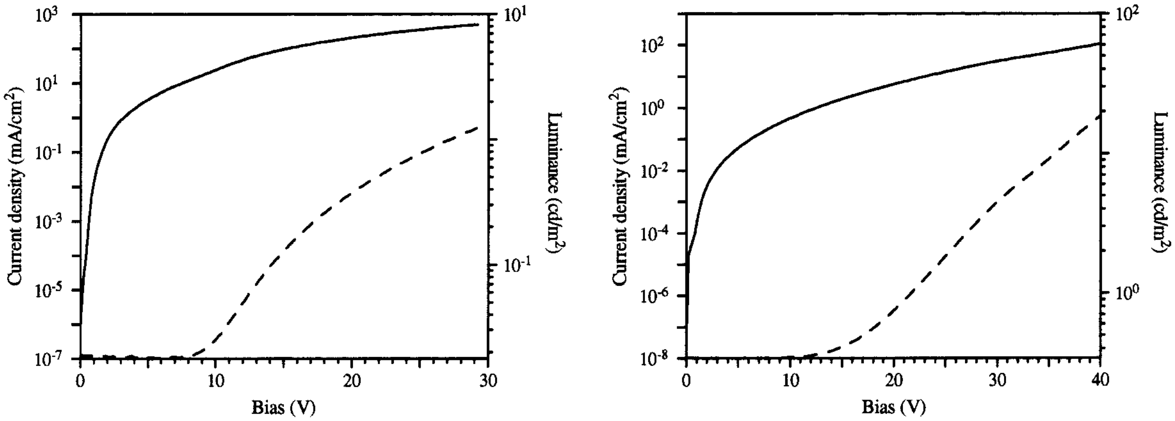

FIGURE 1. (Left) Current (solid line) and luminance for a ZrC/MEH−PPV (1400 Å)/Au device. (Right) Current (solid line) and luminance for an ITO/MEH−PPV (1200 Å)/Al device. Reprinted with permission from ref 22. Copyright 1997 The International Society of Optical Engineering.

taking these images, a gold film was imaged with perfect reproducibility and fidelity. Thus, while surface characterization did identify some poorly conducting material, it appears limited to a few angstroms and is insufficient to prevent facile tunneling injection.

Since the measured work function is roughly the mean of those of Al and Ca, one would expect far better electron injection from ZrC than from Al. Indeed, when devices were made[22] (using Au as the anode and (poly[2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene], or MEH−PPV, as the emitter), it was found that the bias required to obtain light emission (the “turn-on voltage”) was intermediate (Figure 1): about 8 V, as compared to 13−15 V for Al, and ~3 V for Ca (for the same polymer thickness). However, the *efficiency* was far *lower* for the ZrC device than for either of the others: less than 1 mcd/A, compared to 15 mcd/A for Al and close to 1 cd/A for Ca. Various possible explanations for low efficiency such as leakage paths (which carry current but do not produce light) could be ruled out. In addition, it was found that the devices did not function longer under bias: in fact, the order of device lifetime was Ca > Al > Ag ≃ ZrC. The low efficiency and lifetime could be explained by postulating that electrons, injected from a pristine metal into an undoped polymer, quickly become trapped, and these traps are effective luminescence quenching centers. When some doping is present, the charge carriers remain mobile.

These results, consistently with the data of Bröms et al.[16] and Bharathan and Yang,[21] demonstrate that some cathode reaction is desirable for device function: without interface states to lower the barrier, low efficiency is likely even if the work function−LUMO mismatch is small. Parker's[13]data can be qualitatively explained by the fact that the work functions of the metals he investigated correlate reasonably well with their tendency to donate electrons to the polymer. The full explanation cannot be quite this simple, however, because while Ca undergoes a complete charge transfer, Al tends to form covalent (though polar) bonds with the polymer.[14] Thus, what appears to be important is not simply the extent of “doping” (as conventionally understood by electrochemists), but some measure of the degree of polarity of the interface. This aspect of the surface chemistry is still in need of refinement.

Anode. One of our hopes when we began to work with the carbides was that we could use them as STM tips, and thereby analyze charge injection under conditions that were well defined both chemically and spatially. While our results suggest that this may not be feasible for electrons, hole injection involves less reactive materials, and I−V characteristics of MEH−PPV using Pt/Ir STM tips have been obtained in good agreement with the standard film devices. To accomplish this, the sharp, etched tip was first deliberately pushed slightly into a metal substrate to form a relatively flat end with lateral dimensions on the order of 1 μm.[1] Then this tip was brought into tunneling contact with a polymer/ITO sample with the microscope set to zero scan size, 100 pA current, and various biases ranging from 4 to 8 V. The tip was always in contact with the polymer when current flow was obtained, so the physical situation is entirely analogous to the standard device except that pressure is used to contact the top electrode instead of vacuum evaporation. For larger bias setpoints the set current could be obtained with a larger separation between the tip and ITO; for smaller biases the tip pushes further into the polymer and establishes a smaller separation.

By imaging the resulting impression on the polymer with atomic force microscopy (AFM) as shown in Figure 2, the exact lateral contact dimensions as well as film thickness during the STM experiment could be ascertained, and so an I−V curve obtained from the STM could be compared with an I−V obtained on a standard film device. Because both ITO and Pt are relatively high work functions, we assume that only hole current is passed in these experiments. When the STM tip is just barely in contact with the polymer, and the bias is positive on ITO (so that it is the injecting contact), one obtains 5 mA/cm^2 at a field of 1.2 MV/cm; this is in extraordinarily close agreement with Parker's experiments.[13] With the opposite polarity, Pt/Ir is injecting, and the same current density is realized with 0.50 MV/cm, showing that Pt is the better hole injector; this is consistent with its larger work function.

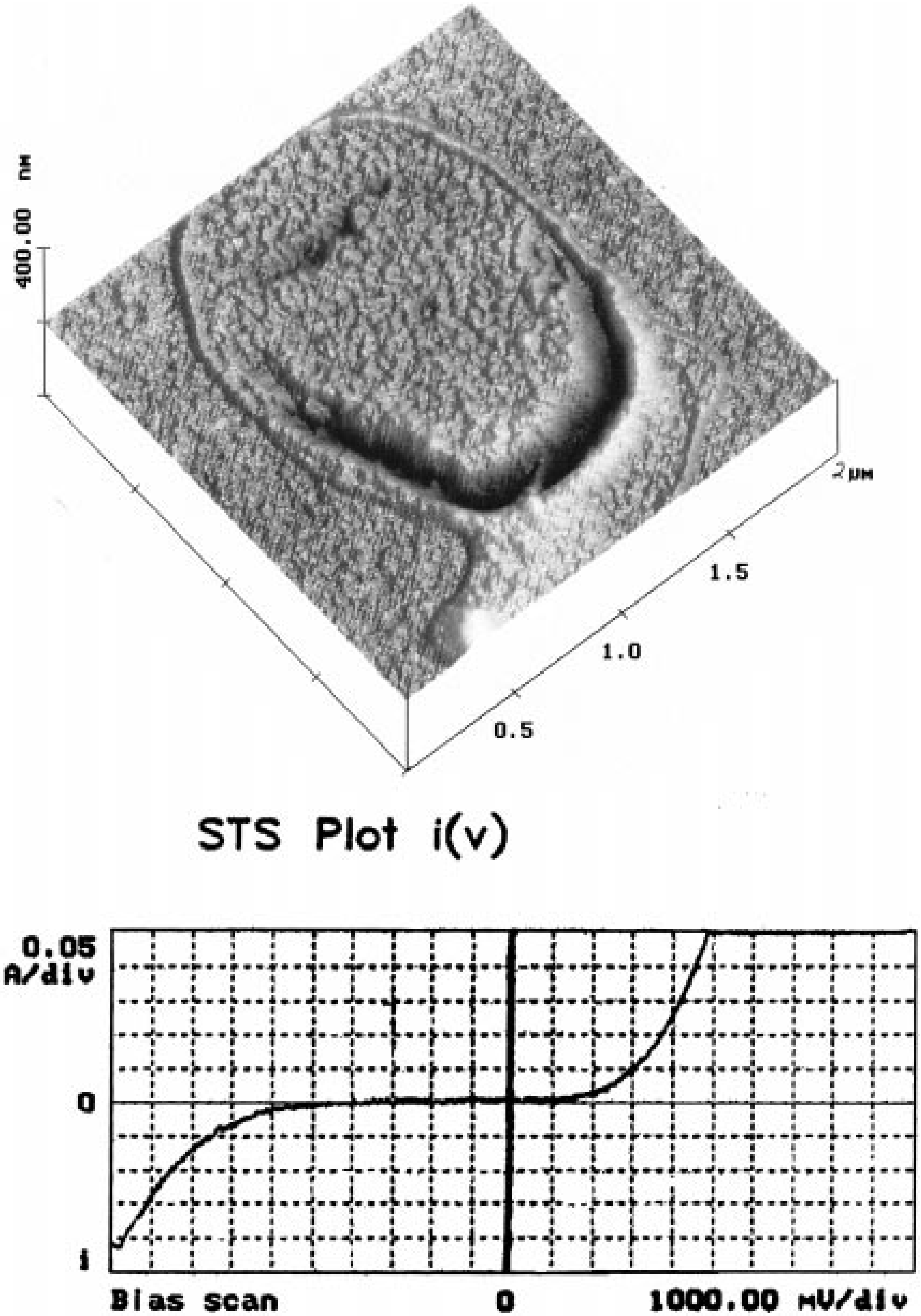

FIGURE 2. AFM and STM data (both from a Digital Instruments Nanoscope III) for an MEH−PPV film on ITO. (Top) AFM image of the indentation made by the STM tip during the electrical measurement shown below. The STM tip was lowered with zero scan size at 8 V and 110 pA until conduction was obtained. The film is 750 Å thick, and slopes from unchanged on one side to about 10 Å lower as the hillock next to the trough is approached; the indentation is about 150 Å at the edge, but partially compensated by the ~50 Å high hillock. To a reasonable approximation, therefore, the average thickness can be taken as 740 Å. The area of the spot is 1.81 μm^2. (Bottom) $I-V$ curve (scanning tunneling spectroscopy mode). The direction of bias is such that the ITO is positive with respect to the tip on the left side.

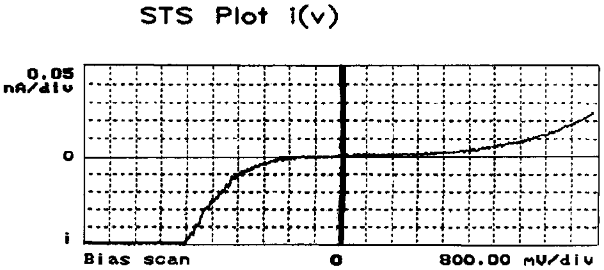

FIGURE 3. STM *I*–*V* curve for a different spot, with 580 Å thickness under the tip.

However, this congenial picture is almost exactly reversed when the tip is pushed substantially into the polymer (200 Å out of a total film thickness of 750 Å) (Figure 3). Thus, either there has been a change in energy levels (work function or HOMO), or the simple work function picture is again no longer valid. Presumably the polymer has been compressed when the tip is pushing on it, and it might be enough to red shift the energy, bringing it closer to ITO and further from Pt. Since the deformation is mainly inelastic, this seems unlikely to be the correct explanation. Alternatively, the polymer chains close to the surface are more aligned (by the hydrodynamics of spin-casting) than those further away;[24] in addition, the tip might even be causing partial alignment of the chains. These aligned chains, by virtue of intermolecular interactions, would have lower energy. While the mechanism has not been definitively established by these observations, the effect of polymer morphology on electrical characteristics is clear.

Alvarado et al. have reported[25] STM-induced luminescence from PPV in a UHV system, in which the PPV was also cured in the UHV chamber. In their case the dependence of EL and current on bias voltage suggests that electrons are injected (through space) into the LUMO of the polymer regardless of the nature of the tip. We believe this difference is due to the degree of oxidation of the polymer surface, which will be zero with complete UHV treatment, whereas our samples were handled in air with some exposure to ordinary room light. This is known to lead to oxidation, and we suggest that the oxidized species are good electron traps which build up a space charge that tends to inhibit further injection.

Ion Migration Effects

Organic EL devices are customarily made using ITO as the transparent electrode. Although this material is usually thought of by electrochemists as relatively stable, indications appeared early in the development of organic EL that it could be the source of degradation.[26]

We have studied[27] the effects of electrical stress (i.e., operation under bias) using time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is especially well suited for the purpose due to its extremely high mass resolution along with the sensitivity of mass spectrometry. Figure 4 shows the indium signal as a function of stress for a polymer EL device on ITO, clearly demonstrating that In moves to the top surface of the polymer. (In these

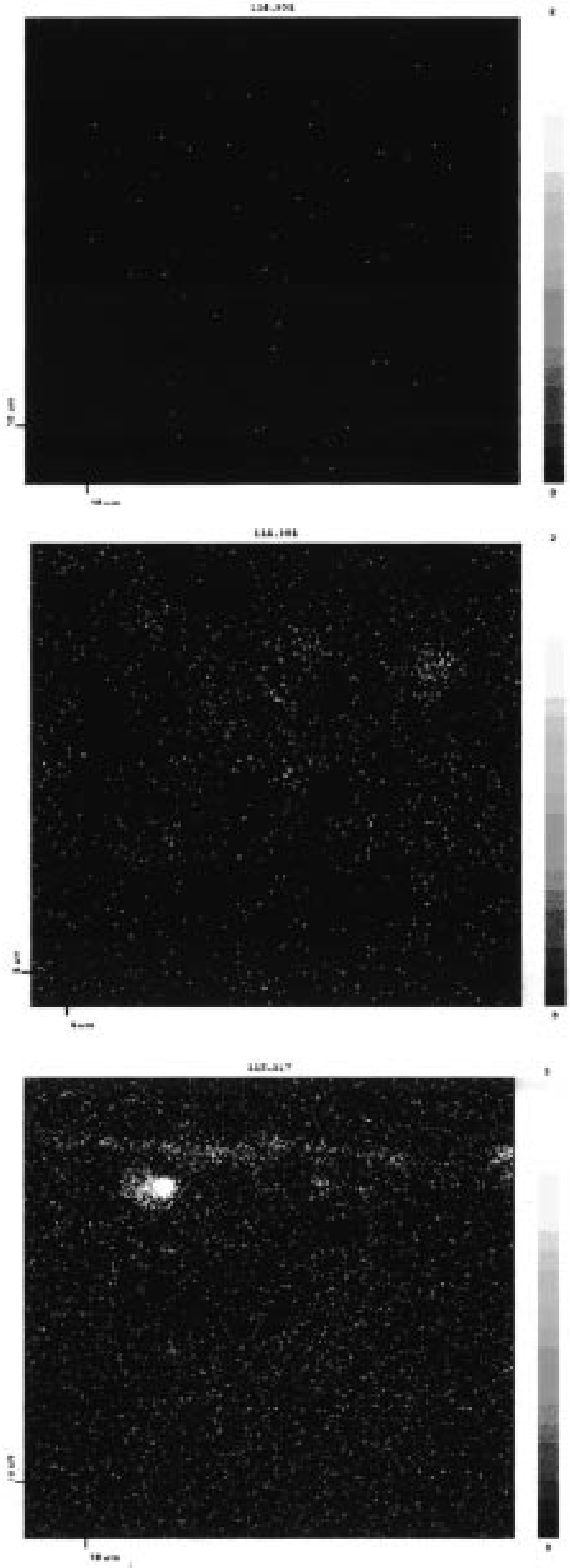

FIGURE 4. TOF-SIMS spatial maps for In in three different polymer LEDs (from which the calcium electrode has been removed with water) subjected to different amounts of electrical stress: none, 1.5 kC/cm^2, and 47.5 kC/cm^2, respectively. The relative positive ion count rates are 0.050%, 0.161%, and 0.481%, respectively. Reprinted from ref 27. Copyright 1999 American Chemical Society.

experiments, the Ca cathode has been washed off with water.) The ITO substrate of such a stressed sample is found to be severely pitted. Thus, it appears that In ions are drawn out of the ITO by the electrical field present during operation, and they then migrate through the film. This happens even with polymers that do not react in any way with ITO (as does the PPV precursor during the curing process[28]). This ionic motion is a likely cause of the electrical leakage often observed: reaction with negative charge carriers reduces the In ion back to In metal, and eventually builds up a short. The problem can be eliminated by addition of a conducting polymer such as polyaniline or polythiophene between the ITO and emitting polymer; this reduces the field at the ITO surface to zero.

Figure 4 shows a noticeable In signal even for no stress, which must come from pinholes (when the same polymer is cast on a Si wafer, a Si signal is seen in a similar manner). There is some uncertainty in the literature concerning whether In will move into a nonprecursor type polymer without any electrical stress; one report suggests that it does.[29] Our results do not rigorously exclude such a process, but they also do not require it, and are most parsimoniously explained without it.

Similar measurements made after removing the polymer with toluene show that Ca is found on the ITO surface, where it most likely arrives through pinholes. As a function of stress it gradually disappears, as is expected from the direction of the applied field.

Chemical Degradation

Information pertinent to the polymer can be gained by examining the Ca signal[27] on the polymer surface, as shown in Figure 4d−f, which shows the growth of signal intensity with the amount of stress. Thus, some reaction has occurred (as a consequence of electrical operation) that results in a species capable of binding Ca and holding it despite copious washing of the surface with water. It must be negatively charged (after exposure to water and air), and it must be related to electrical operation (i.e., it does not result from diffusion of impurities to the surface). If injected electrons are trapped (by oxygen-containing sites or by other polymer defects), scenarios for the transformation of these species (on air exposure) to stable oxygenated sites that could bind calcium are readily envisaged. More precise identification of the initial reaction products (e.g., by avoiding water exposure) is quite difficult: depth profiling by ion bombardment of inorganics on organics typically leads to substantial interface mixing and resulting uncertainty. A surface chemical reaction associated with device degradation has, nevertheless, been unambiguously demonstrated.

Given the power of TOF-SIMS to provide identification of large molar mass fragments, we attempted to find evidence of new organic species directly. While the identification of each of the many peaks in the spectrum is a tedious process without an appropriate analysis program, one can at least make a comparison between the spectra for different amounts of electrical stress. For the same sample as is used in Figure 4 (which is poly(9,9′-dioctylfluorene-*co*-9-octyl-9′-(*tert*-butyldimethylsiloxyphenyl)fluorene), 10:1; denoted PFSE), we have carried out such a comparison on the positive ion spectra (after normalizing, as usual, to the total ion yield for each case). In general very few peaks change intensity significantly (i.e., by an amount greater than the variation of two spectra of the same sample), with two noteworthy exceptions. First, the Si-containing peaks in the heavily stressed sample are about half as large (indicating loss of the trialkylsilyl ether). Second, the higher mass fragments (greater than about 200 m/e), though having small intensities in either case (typically several counts out of $>10^6$), are much more numerous for the heavy stress case (new peaks appear, and many existing ones are more intense). A similar observation holds for the high-mass negative ions.

Thus, there is definite evidence of some chain breakage, or other chemical reaction that makes ion-induced breakage easier, but the actual amount of this damage appears to be in the parts per million regime. Thus, a straightforward decrease in molecular contour length (i.e., a “falling apart” of the polymer) is not a significant factor in device degradation, nor did we find evidence of metal ions (other than In) or small organic molecules (with important fragments of $m/e < 100$) migrating to the surface. The results instead suggest functional group transformations that serve as charge traps and luminescence quenchers. Charge trapping, even on the parts per million scale, is known to have major effects on both injection efficiency and luminescence yields.[3,30] This conclusion is in accord with the Ca binding data in Figure 5.

During the early development of organic EL devices, a great deal of attention was given to photooxidation,[31] since conjugated polymers such as PPV are especially prone to this reaction (the commonly used molecular emitter Alq_3 photooxidizes about 10 times slower). It was shown that concentrations of carbonyls down to around 0.1 mol % led to detectable PL quenching; below that level no effect was found.[31] We wanted to ascertain if EL lifetimes were affected by oxidation. In general, the TOF-SIMS spectra have shown somewhat *smaller* intensities of the O negative ion for stressed samples. For example, in the unstressed sample of Figure 5 the yield is 1.8%, and for the heavily stressed sample 1.1%. The most likely explanation for this is a SIMS matrix effect: the greater amount of Ca reduces the negative oxygen ion yield.

We have found, however, that surface oxidation is indeed deleterious to device operation. When either PFSE or poly(9,9′-dihexylfluorene) (PFH) was photolyzed in air (380−425 nm excitation), fluorescence slowly decayed (more rapidly for PFSE) and the oxygen peak intensity in PFH TOF-SIMS spectra increased proportionally. Devices made with photolyzed polymers ($\sim$7−25 J/cm^2, a dose that is barely detectable by eye in fluorescence) gave less current and light at a fixed voltage compared to those without irradiation. While efficiency was modestly reduced (by 40% in PFSE, marginally if at all in PFH), the current

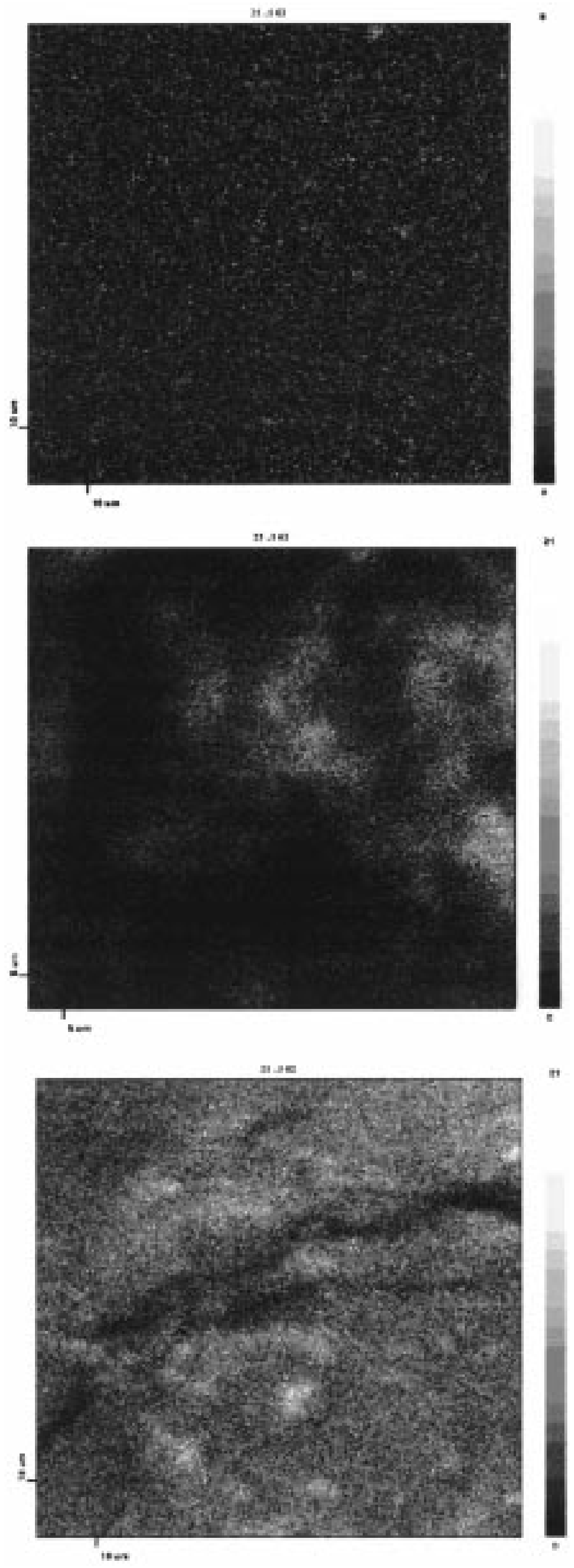

FIGURE 5. Same as for Figure 4, but for Ca. The relative ion counts are 0.063%, 0.14%, and 0.25%. Reprinted from ref 27. Copyright American Chemical Society.

was reduced about 5-fold in PFSE and close to 2-fold in PFH. This is the expected trend if oxygen moeities behave as electron traps.

Summary and Conclusions

Both empirical development and scientific understanding of chemical processes in operating organic EL devices have progressed dramatically during the last 6 years. For hermetically sealed devices, state of the art lifetimes (defined as the time to 50% of initial output, at constant current) today are well over 10 000 h at the prototypical luminance of a computer display (100 cd/m^2). For certain types of PPV devices that pass primarily hole current, the lifetime appears indefinite (i.e., no degradation has occurred after more than 10 000 h).[32] This, combined with the fact that photostability in the absence of oxygen is extremely good (quantum yield around 10^{-9} or less),[9] strongly suggests that at least for one important class of materials, reactions involving the negative charge carriers are the critical problem. On the other hand, specific reactions at the cathode interface appear essential to obtain good electron injection. More extensive studies with TOF-SIMS, especially using oligomers with well-defined molar masses, could go a long way toward more fully elucidating the reactions that accompany degradation of light output, and provide a basis for molecular design principles that would reduce it. With some further progress in device lifetime, increased efficiency obtained by better light extraction techniques, and the remarkable manufacturing cost reductions that are expected from the development of roll to roll processing, organic EL may achieve commercial success in the entire range of applications where moderate average luminances are required. This development will be complementary to the revolution in high-intensity solid-state lighting based on inorganic LEDs.[1]

We are indebted to William Mackie for his very helpful collaboration, Ron Moon for his support, and Homer Antoniadis and Mark Hueschen for many valuable conversations. A.S. was funded by the HP Labs Grassroots Basic Research Program. The polyfluorenes were kindly supplied by E. Woo and colleagues at Dow Chemical Co., and the MEH−PPV was provided by Uniax Corp.

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AR980061Q