Macromol. Symp. ***125,*** *83–97 (1997)*

METAL INDUCED PHOTOLUMINESCENCE QUENCHING OF A PHENYLENE VINYLENE OLIGOMER AND ITS RECOVERY

Vi-En Choong*, Yongsup Park, and Yongli Gao

Department of Physics and Astronomy, University of Rochester,
Rochester, NY 14627 , U.S.A.

Bing R. Hsieh

Xerox Corporation, Joseph C. Wilson Center for Research &
Technology, 114-39D, Webster, NY 14580 , U.S.A.

Ching W. Tang

Imaging Research and Advanced Development, Eastman Kodak
Co., Rochester, NY 14650 , U.S.A.

Abstract :
Metal/polymer interfaces play an important role in polymeric light emitting diodes (LEDs). In typical organic light-emitting devices, metallic electrodes are used to inject charged carriers into the organic electroluminescent (EL) medium. However, what other effects the metals have on the organic medium is not well known. In this work, we report severe photoluminescence (PL) quenching of organic thin films comprising of one of the most useful materials, namely 1,4-bis[4-(3,5-di-tert-butylstyryl)styryl]benzene (4PV), upon sub-monolayer deposition of Al, Ag, and Ca in an ultra high vacuum environment. The severity of the luminescence quenching may greatly affect the EL device performance. Gap states at the Ca/4PV interface are shown to be responsible for the PL quenching. The oxidation of Ca resulted in the removal of the gap states and the recovery of the quenched PL.

INTRODUCTION

When one thinks of organic materials, flexible, and easily processible materials having electrically insulating properties typically come to mind. However, some organic materials have been found to possess the electrical and optical properties traditionally associated with metals and semiconductors, while retaining the mechanical properties mentioned above. This combination of electrical and mechanical properties has attracted a good deal of fundamental scientific interest. The use of organic materials in molecular based electronics, such as light emitting diodes (LEDs), is relatively new (Ref. 1, 2, 3, 4, 5), and lends weight to the importance of careful characterization of these materials. One of the key issues for the organic semiconductors to be useful is the understanding of interfaces, since

CCC 1022-1360/97/$ 04.00

organic devices consists of thin film structures with typical effective thicknesses of the order of 100 nm. Thus, the distinction between the bulk and the interface is blurred. The demonstration that a multilayer structure is critical to the improvement of device performance further emphasizes the importance of interfaces (Ref. 6, 7). Injection electroluminescence (EL) has been demonstrated in numerous organic materials ranging from tris-(8-hydroxyquinoline) aluminum (Alq_3) (Ref. 6, 8), a sublimable compound, to poly(p-phenylene vinylene) (PPV) (Ref. 9), a conjugated polymer. The device structure generally consists of, in sequence, an indium tin oxide (ITO) covered glass as the anode, a thin layer (or multiple layers) of organic materials, and an evaporated metal film as the cathode.

The efficiency of these EL devices has been found to be highly dependent on the injection behaviors of the contacts (Ref. 10, 11, 12), limited primarily by the electron injection efficiency of the cathode (Ref. 13, 14, 15, 16). Presumably, a lower electron injection efficiency from the cathode would result in an injection current dominated by the holes in the organic layer and consequently the electron-hole recombination would occur at or near the cathode surface (Ref. 17, 18). The role of the metal electrode as merely an agent for charge injection has been challenged by our recent observation (Ref. 19) that the photoluminescence (PL) of 1,4-bis[4-(3,5-di-t-butylstyryl)styryl]benzene (4PV, Fig. 1 inset) can be severely quenched by the deposition of Ca, a metal known as a superior cathode for PPV based EL devices due to its low work function. The fact that the measured spectra for both EL and PL are basically identical implies that both processes are due to the same emissive species. Consequently, the observation of metal-induced PL quenching may be important for single-layer LEDs. This is particularly significant for PPV based LEDs since the recombination region is near the metal cathode due to its hole conducting nature.

At a metal/organic interface, charge transfer from the metal to the organic material may induce gap states associated with lattice deformation of the organic material (Ref. 20, 21) The formation of such gap states, termed polaron and bipolaron states, has been experimentally observed (Ref. 22, 23, 24) and causes energy level bending in the organic material near the interface (Ref. 20, 21, 25, 26). However, the effect of these states on the luminescence properties of organic materials has not been explored. In this paper, we report our systematic investigation to characterize the luminescence quenching phenomenon using Ca, Al, and Ag on 4PV in an ultra high vacuum (UHV) environment. Ca, Al and Ag were chosen because they are frequently used as cathodes in EL devices. Furthermore, 4PV can be sublimed to form an impurity-free thin film in UHV, thus allowing a molecularly clean surface not possible for PPV. We observed that deposition of all three metals on the 4PV layer produced dramatic luminescence quenching even at sub-monolayer coverages, suggesting that metal quenching may critically affect the efficiency of organic EL devices. Similar quenching processes are also observed for Alq_3, which is one of the most representative light emitting organic molecule. We also present evidence that the formation of gap states upon Ca deposition is responsible for the observed PL quenching in 4PV. The recovery of the PL upon removal of these states will also be discussed.

EXPERIMENTAL

The synthesis and basic photophysical properties of 4PV are described in detail elsewhere (Ref. 27, 28, 29). We used ultraviolet photoelectron spectroscopy (UPS) to probe the valence electronic structure of Ca/4PV at the University of Rochester. The entire PL and UPS experiments were performed in a UHV chamber with the base pressure of 1×10^{-10} Torr. The thickness of the 4PV films was 300 Å. The films for the UPS experiments were deposited on Au coated Si substrates while those for PL were deposited on ITO coated substrates through thermal evaporation in UHV at a rate of approximately 2 Å per minute. The evaporated sample was then transferred to the analysis chamber *in situ* for PL and UPS data acquisition as well as metal deposition (the deposition rate was approximately 1.0 Å per minute). The deposition rates were monitored by a quartz crystal microbalance. No dectable impurity was found for the deposited 4PV films as observed by x-ray photoemission spectroscopy (XPS). An Oriel 77501 fiber-optic light source with a regulated lamp was used to produce the excitation light for PL, which went into the UHV chamber through a quartz window. The excitation wavelength was chosen using a Carl Zeiss M4QIII prism monochromator. The excitation wavelength used was 400 nm, since it produced the highest level of luminescence for 4PV. The PL data was recorded with a Photo-Research SpectraScan 650 photo colorimeter. The UPS spectra were taken with a 21.2 eV He I discharge lamp and a hemispherical electron energy analyzer. This combination resulted in an overall energy resolution of 0.2 eV. The oxygen exposure was performed by filling the vacuum chamber with pure (99.999 %) oxygen gas at the pressure of 5×10^{-6} Torr. The exposure was measured in the unit of Langmuir (L) which is defined as 1×10^{-6} Torr sec. The sample was kept in darkness during the exposure to eliminate possible contributions to the PL quenching due to photo-oxidation and the formation of carbonyl groups in 4PV (Ref. 30).

RESULTS AND DISCUSSION

The PL spectra of 300 Å 4PV on an ITO substrate at various Ca coverages, Θ, are shown in Fig. 1. The shape and the position of the peaks are consistent with those obtained by Woo *et al.* (Ref. 29). The observed PL quenching is very severe as indicated by the fact that even the deposition of 0.1 Å Ca reduces the PL intensity by 50%. However, there is no noticeable change in the spectral shape. Further deposition of Ca continues to quench the PL although the effect is more gradual than that of the first 0.1 Å. Figure 2 is the PL intensity plotted as a function of Θ. The rate of intensity decrease can be divided into three stages. The first stage, more clearly seen in the inset of Fig. 2, is between Θ = 0 and 1 Å. The second stage is between Θ = 1 and 30 Å, and the third for Θ > 30 Å. The rate of decay is highest in the first stage and lowest in the third stage.

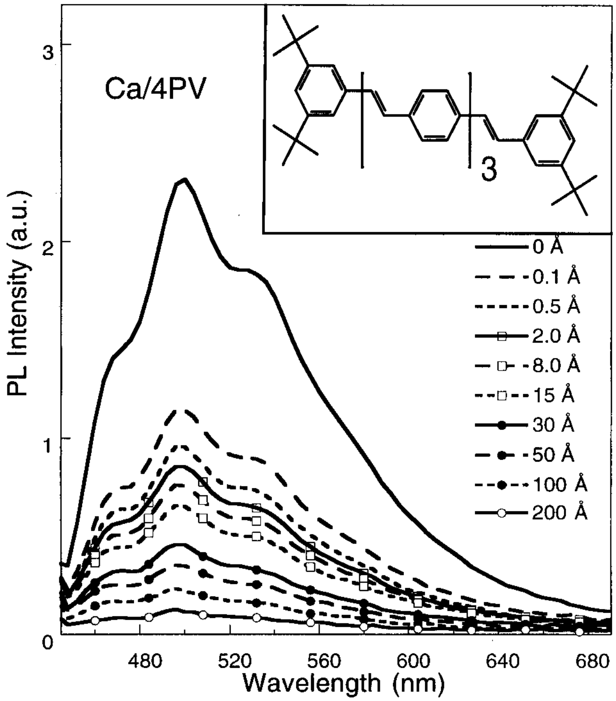

Fig. 1 The PL spectra of 4PV on an ITO substrate for various Ca coverages Θ. The inset shows the molecular structure of 4PV.

PL intensity is reduced by 65 % in the first stage alone. At least three possible mechanisms are responsible for the dramatic PL quenching. First, this decrease could be due to Ca induced energy level bending which splits the excitons apart, resulting in lower yields. Second, a strong chemical reaction between Ca and 4PV may have occurred, yielding products which effectively quenches the luminescent species. Third, the Ca atoms provide nonradiative decay routes. Our previous XPS studies (Ref. 25) of the interface formation between Ca and 5PV have shown that the Ca induced energy level bending is completed at a much larger value of Θ than 1 Å, and since the same XPS studies did not show any evidence of a strong chemical reaction between Ca and 5PV, mechanism (1) and (2) can be ruled out. Therefore, we attribute the initial drop in intensity to mechanism (3), nonradiative decay channels created by the deposited Ca. The charge injection from the Ca atom into 4PV may induce the formation of radical anions or polarons, acting as dissociating centers for photoinduced excitons (Ref. 31).

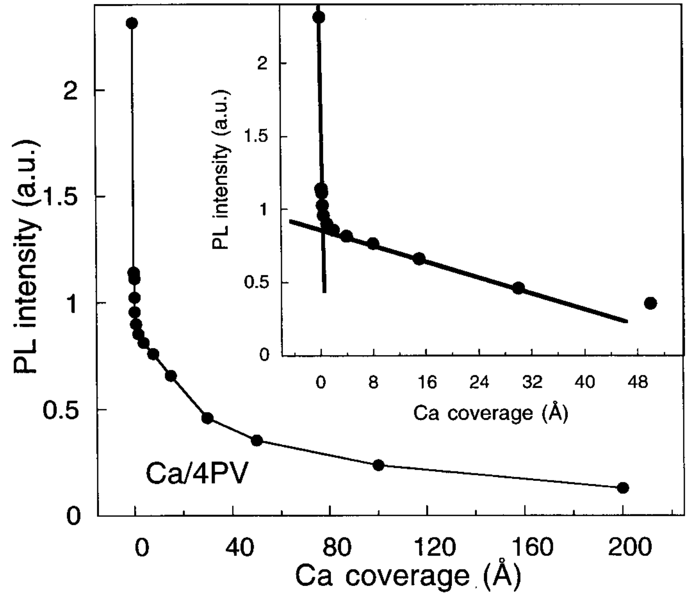

Fig. 2 The evolution of PL peak intensity as a function of Ca coverage, Θ. The inset emphasizes the first and second stages.

After the initial drop, the effect of PL quenching by Ca atoms is reduced, as indicated by a slower rate of PL quenching observed in the second stage. This can be explained by a rather simple argument. Consider a surface with several Ca atoms. Each Ca atom has a certain "quenching radius" defined by the exciton diffusion length within which any exciton created will be quenched. Therefore, any additional Ca atoms added within the quenching radius of an existing Ca atom will have a lesser effect than it would have if it were deposited on a clean surface. This picture may be complicated by the fact that Ca may diffuse into the near surface region of 4PV just as has been reported for poly(2,5-diheptyl-1,4-phenylenevinylene) (DH-PPV) (Ref. 32), and by the possibility of contributions from the Ca induced energy level bending process. However, if Ca diffuses extensively into 4PV, we would expect its density inside 4PV to be linearly proportional to the amount of Ca deposited, leading to total quenching of the PL at $\Theta = 0.2$ Å. We have also investigated the time dependence of the PL quenching at a given Ca coverage, and observed no detectable change in the course of more than 10 hours. This is again inconsistent with a diffusion picture which is a time dependent process.

In the third stage, $\Theta > 30$ Å, we attribute the drop in PL intensity solely to the attenuation of both excitation and emission photons due to the thickness of the Ca layer, since the Ca layer becomes bulk metallic at approximately 30 Å coverage as observed in our XPS studies.[17] At this point, we expect that the coverage of Ca is such that the PL quenching is saturated. A simple curve fit of our data in this region employing the following formula: $I(\Theta) = I(0)\exp(-2\Theta/\zeta)$, where $I(\Theta)$ is the PL intensity at coverage Θ and ζ is the attenuation length, yielded 290 Å for ζ. The factor of two in the exponential takes into account the fact that both the incident excitation and the emitted light had to pass through the Ca overlayer. The ζ value obtained here corresponds quite well with the calculated value for a typical metal, which is of the order of 100 Å (Ref. 33, 34).

The PL intensity of 4PV samples with different 4PV layer thicknesses plotted as a function of Θ, shown in Fig. 3, confirms that Ca indiffusion is limited in the time frame of our experiment. The lines in Fig. 3 are not curve fits, but just a guide for the eye. If Ca indiffusion was extensive, it would be reasonable to expect that the percentage of the quenched PL intensity to be independent of the thickness of the sample. However, this is not the case as shown in Fig. 3. Given that Ca indiffusion is limited, and neglecting the quenching effect of the ITO substrate, it can be estimated from the 65% reduction of the PL intensity of the 300 Å thick sample that the light emitting species within the top 200 Å of the film has been quenched. Similarly, we find that the apparent quenching thickness, Δ, is 200 Å and 127 Å for the 500 Å and 150 Å films, respectively. The fact that $\Delta_{Ca} = 200$ Å for both the 300 Å and 500 Å films proves that the Ca indiffusion is limited. In fact, the independence of Δ_{Ca} on the thickness of the 300 Å and 500 Å 4PV films, and the observed change of the slopes of the quenching curves indicate that the penetration of Ca into 4PV, if there is any, is not well explained by a diffusion process which is described by a time dependent linear equation. The above is better explained by substrate disruption due to the release of condensation energy when Ca atoms impact the organic film. We believe that PL quenching by the ITO substrate is negligible, since we were able to observe PL for a 20 Å 4PV layer on ITO. The quenching thickness of 200 Å can therefore be attributed mostly to the exciton migration distance, which is much greater than the size of a 4PV molecule (2 x 8 x 40 Å). For the 150 Å 4PV film, intuitively, one would expect its luminescence to be completely quenched from Δ obtained from analysis of the 300 Å and 500 Å films. However, luminescence was still observed in the 150 Å film. Several factors may have contributed to this. One factor is the roughness of the glass substrate. Such roughness may noticeably alter the local thickness for the 150 Å film. The morphology of the 150 Å film may also be affected by the substrate to a greater degree than that of the thicker films. Furthermore, although the average exciton migration distance is ~200 Å, it is reasonable to expect that some excitons will recombine radiatively before traveling that distance.

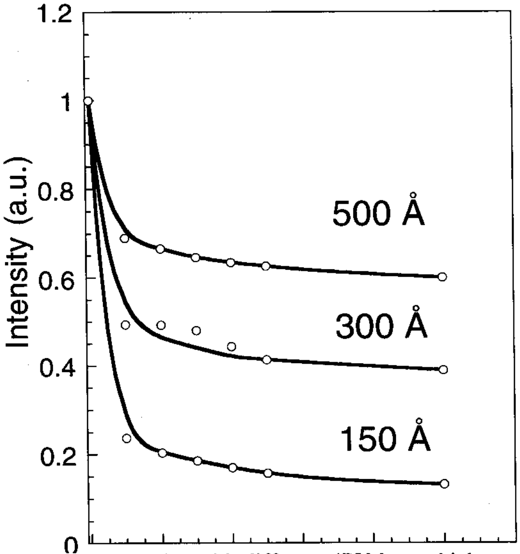

Fig. 3 The PL intensity of 4PV samples with different 4PV layer thicknesses plotted as a function of Ca coverages, Θ.

Figure 4 shows the PL intensity as a function of the thickness of the 4PV film, Φ, on two substrates, (a) Ca, and (b) ITO. For the Ca substrate, the PL was not visible until approximately Φ = 125 Å, but was not measurable until Φ = 150 Å. Only after Φ = 200 Å did the PL increase linearly with Φ. The late onset of the PL is attributed to the quenching of the emitting species in the 4PV layer by Ca. The extrapolation of the linear part of the PL intensity curve to the x-axis yields Δ_{Ca} = 145 Å (dashed line in Fig. 4). It is reasonable to assume that 4PV does not diffuse into Ca. By comparing this value for Δ_{Ca}, and our previously estimated value, Δ_{Ca}= 200 Å (Fig. 3.), we can estimate that the deposited Ca disrupts the 4PV layer to a maximum extend of 50 Å. This is consistent with the values previously reported in the literature (Ref. 32). The situation for the ITO substrate is very different from that for the Ca substrate. The PL was measurable as early as Φ = 20 Å when

ITO was used as the substrate and even at low Φ, the PL was increaseing linearly with Φ. Furthermore, an extrapolation of this linear part of the PL intensity curve to the x-axis yields $\Delta_{ITO} = 0$ Å indicating that ITO does not quench the PL of 4PV. Thus, the PL quenching phenomenon does not depend on whether a material is conducting. This raises the question of whether this quenching phenomenon is unique to Ca, or common among all metals.

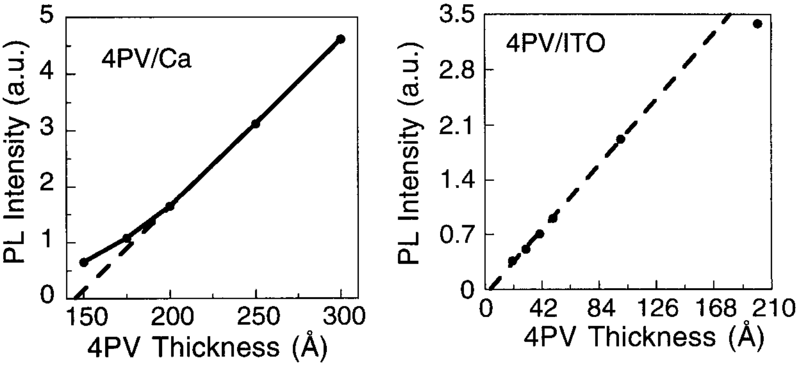

Fig. 4 PL intensity as a function of the thickness of the 4PV film, Φ, on two substrates, (a) Ca, and (b) ITO.

The PL intensities plotted as a function of coverage, Θ, of Ca, Al and Ag on 300 Å 4PV films are shown in Fig. 5. The behavior of the PL as a function of coverage is similar for all three metals even though their workfunctions differ by as much as 2 eV. Furthermore, our data presented above suggests that ITO does not quench the PL of 4PV even though it is conducting, and its workfunction is comparable to that of Al, and Ag. This suggests that the PL quenching is indeed common to metals and is relatively insensitive to the details of the energetics of the particular metals used. This is puzzling since the bulk of the quenching occurs before there are sufficient metal atoms for the metals to exhibit their bulk metallic nature. However, with the present data, we are not able to answer this question.

We performed repetitive Ca deposition and oxygen exposure cycles up to 50 Å with incremental Ca thickness. The PL spectra were taken before and after Ca deposition, and after exposure to 5×10^{-6} Torr of O_2 for 5 minutes (1.5×10^{3} L), 30 minutes (1.05×10^{4} L), and several hours (~10^{5} L). This process was repeated on the same sample at several different total Ca thickness (0.1, 1.0, 4.0, 8.0, 15, 30, and 50 Å). Figure 6(a) shows the evolution of PL intensity as a function of Ca deposition/oxidation cycles. The horizontal axis indicates the accumulated oxygen exposure in L and the total Ca thickness is indicated in the figure. As reported previously (Ref. 19), the dramatic quenching (~ 50 %) of the PL intensity is clearly observed. However, the PL intensity recovers back to about 65 % of the pristine 4PV

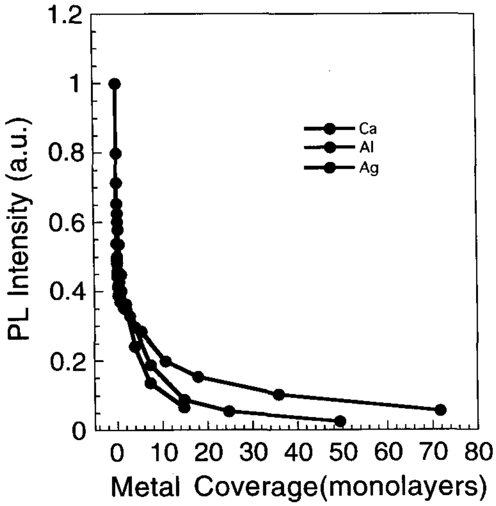

Fig. 5 PL intensities plotted as a function of coverage, Θ, of Ca, Al and Ag on 300 Å 4PV films.

value after the sample was exposed to O_2 for 4.5 hours at 5 x 10^{-6} Torr (8.1×10^4 L). Also at Ca coverages less than 8 Å, the fresh deposition of Ca still greatly affects the PL even though the previously deposited and oxidized Ca separated the freshly deposited Ca from the 4PV. This indicates that the oxidized Ca underlayer in this thickness regime cannot protect 4PV from Ca-induced PL quenching. However, when the oxidized Ca layer thickness approaches approximately 30 Å, additional Ca deposition does not substantially affect the PL intensity. This indicates that the thicker oxide layer is indeed effectively protecting the 4PV from the PL quenching effect of freshly deposited Ca.

The crucial role of the oxidized Ca layer is clearer when we compare the PL intensity evolution with and without the oxidation process, as shown in Fig. 6(b). The bottom curve of Fig. 6(b) is the PL intensity as a function of Ca thickness without the oxidation process. Here a monotonic intensity decrease is evident (Ref. 19). The middle curve is the PL intensity after each fresh deposition of Ca on previously oxidized Ca/4PV. For example, the data point at 8 Å is the PL intensity after 4 Å of fresh Ca was deposited on 4 Å of oxidized-Ca/4PV. The middle curve shows how effective a given Ca oxide layer is in protecting 4PV PL from fresh Ca. The top and middle curves are taken from data shown in Fig. 6(a). In the early stages of Ca deposition (< 4 Å), the middle curve is almost identical with the bottom curve indicating that the existence of a very thin (< 4 Å) oxidized Ca layer has no effect on the changes in PL upon additional deposition of fresh Ca. However, it is obvious that a

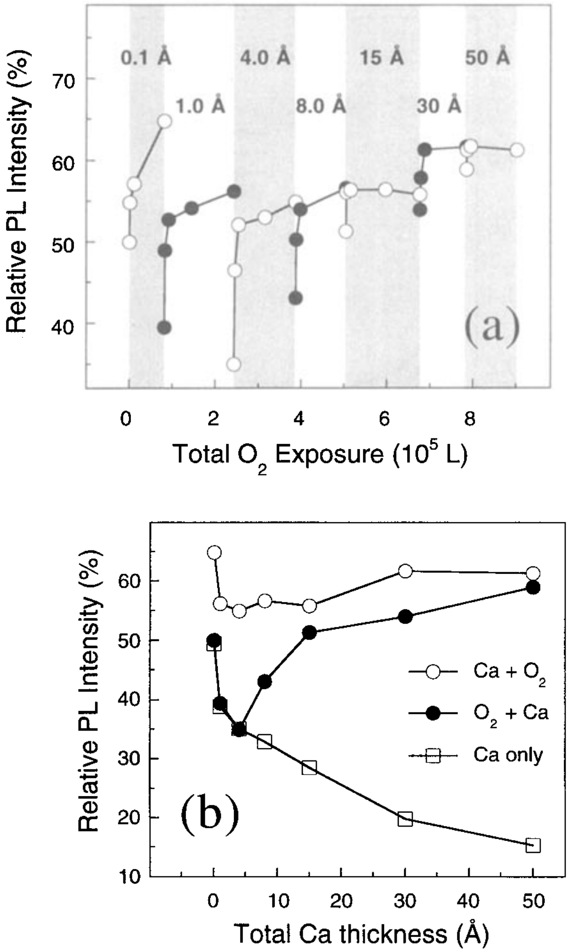

Fig. 6 (a) PL intensity under a sequence of Ca deposition and oxidation cycles. The horizontal axis is the accumulated oxygen exposure. The connected circles indicate the PL recovery process upon oxidation at the Ca thickness indicated. (b) The PL intensity taken with respect to Ca thickness under three different conditions. The bottom curve shows the PL quenching process without the exposure to oxygen.

thicker Ca oxide layer, about 30 Å, effectively protects the 4PV layer from further PL quenching. The top curve in Fig. 6(b) shows the PL intensity at the end of the oxidation process at a given Ca thickness. The PL intensity of oxidized Ca/4PV remains between 55 and 65 % of that of pristine 4PV up to 50 Å of oxidized Ca layer. On the other hand, the PL from unoxidized Ca decreases down to around 15 % after deposition of 50 Å Ca (Ref. 19). These numbers suggest that a proper oxidation of Ca at the Ca/4PV interface could significantly improve the efficiency of a single layer EL device.

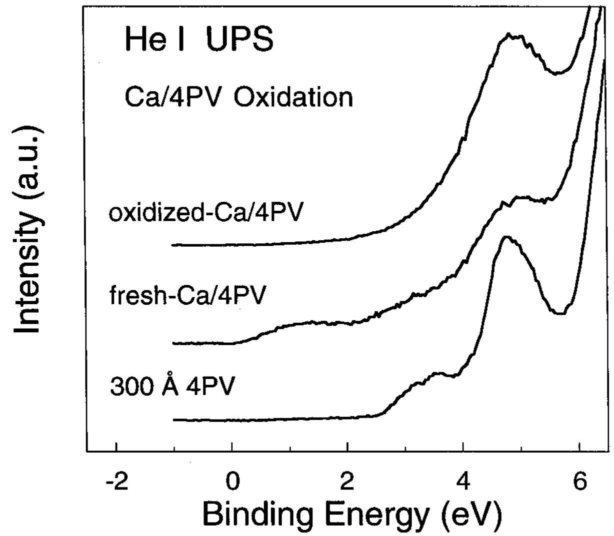

Fig. 7 The changes in UPS spectra upon Ca deposition and oxidation. The bottom curve shows the valence band spectrum of 300 Å pristine 4PV film. The middle curve is when 4 Å of Ca was deposited on the 4PV film. The formation of states in the energy gap region is clearly observed. The top curve shows the same valence band spectra but after oxidation by $9.1x10^3$ L of exposure.

The UPS spectra near the Fermi level for a pristine (300 Å), fresh-Ca/4PV, and oxidized-Ca/4PV ($9x10^3$ L) are shown in Fig. 7. The spectrum of the pristine 4PV sample exhibits the highest occupied molecular orbital (HOMO) feature near 2.4 eV (Ref. 26), and is consistent with that reported for PPV (Ref. 35). Upon deposition of 4 Å of Ca, a broad peak near 1.2 eV was clearly observed. This feature indicates the formation of new states inside the energy gap is clearly observed (Ref. 11, 22, 23, 24). Such gap states have been attributed to the formation of bipolarons via charge transfer from the metal to the organic material (Ref. 22, 23, 24, 25) However, when the fresh-Ca/4PV sample was exposed to oxygen, the gap states completely disappeared as seen in the top curve of Fig. 7. This is strong evidence that the formation and disappearance of gap states may be responsible for the observed PL quenching and recovery, respectively. One possible scenario for gap-state induced PL quenching is depicted in Fig. 8. The bound electron-hole pairs (excitons or polaron excitons) are initially excited by an external radiation. During the lifetime of the exciton, it diffuses an average distance of approximately 150-200 Å (Ref. 19). The deposition of Ca created a region of 4PV near the surface where excess charges from Ca formed occupied gap states. When a migrating exciton encounters this region, the hole can jump to the filled gap states and give the excess energy to the electron. This results in the dissociation of the exciton. In this way the PL is quenched. This process is similar to the PL quenching observed in acceptor doped conjugated polymers (Ref. 31, 36, 37, 38, 39). The oxidation of Ca atoms then withdraws these excess charges from 4PV. This removes the gap states in 4PV, Fig. 7, resulting in an increase in PL intensity.

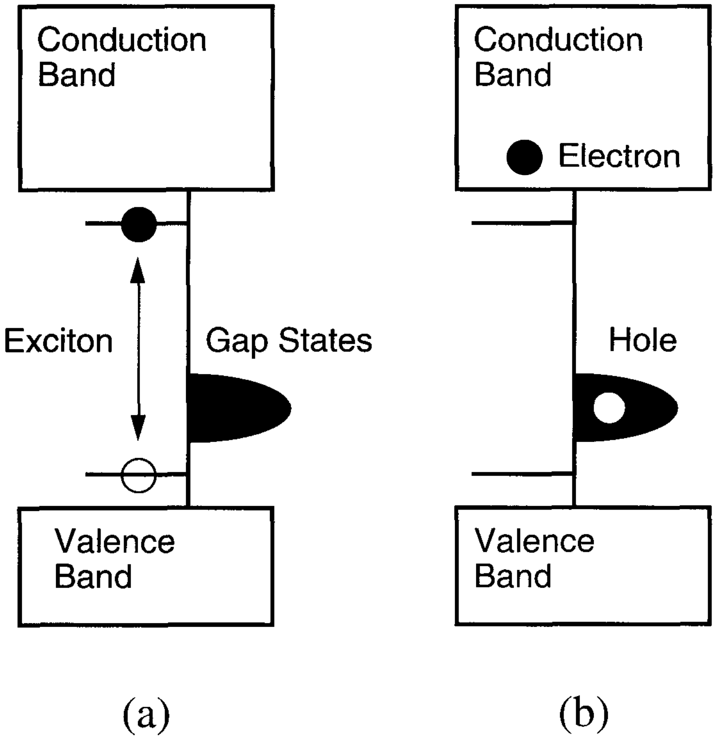

Fig. 8 A simple energy diagram near the Ca/4PV interface depicting the exciton dissociation process in the presence of gap states. (a) The exciton is away from the doped region. (b) After the exciton dissociation has occurred, the electron moves to a higher energy state in the conduction band in order to conserve the pair energy (Ref. 31).

What we have observed suggests that an organic LED, employing a hole transporting material as an active layer and a Ca metal layer as the electron injecting electrode, would perform with higher efficiency when 30-50 Å of the metal layer at the Ca/organic interface was simply oxidized before the rest of the electrode was deposited. However, this is contingent on whether such a layer would greatly hinder the carrier injection. From our results, we could expect that an LED based on a 300 Å thick 4PV layer will exhibit nearly four times efficiency improvement. There have been several reports that suggest improvement in EL performance by introduction of a foreign layer between the active layer and the electron injecting electrode. Bröms *et al.* reported (Ref. 40) that PPV based EL devices with a *dirty* Ca electrode fabricated in 10^{-6} Torr of oxygen partial pressure performed better than the one fabricated in UHV (10^{-10} Torr). Although no correlation between the changes in oxidation-induced electronic structure and enhanced EL performance was suggested in their work, the existence of such a correlation is clear from our results. In addition to suppressing exciton dissociation, the oxide layer (an insulating layer) may facilitate charge carrier confinement in the active layer of EL devices, further enhancing the performance. This was demonstrated by Kim *et al.*, who inserted an insulating layer of poly(methyl methacrylate) (PMMA) between the PPV layer and the Al electrode (Ref. 41). They showed that their EL device performed best when the PMMA layer thickness was about 60 Å. Judging from the measured threshold voltage, the PMMA layer of this thickness did not affect the electron tunneling efficiency. Another example is a polymeric LED consisting of multiple bilayers of alternating active and insulating layers (Ref. 42). When the multilayer was terminated by the insulating layer on which the metal electrode was deposited, the LED performed better than when the multilayer was terminated with the active layer. In view of these reports, it is clear that a foreign non-metallic layer at the interface between the metal and the active EL layer enhances the device performance by avoiding metal-induced quenching of excitons.

Finally, the PL of our 4PV thin films did not recover to its initial value even after prolonged exposure to oxygen. There are several possible origins for the final PL loss of 35 %. First, although we took extreme care not to expose the sample to light and oxygen at the same time, the oxygen molecule may have adsorbed on the sample and later reacted with 4PV when the light was available. This would create PL quenching centers, such as carbonyl groups. Secondly, metal deposition could induce structural changes in the organic layers or the deposited Ca could disrupt and be buried in the 4PV. PL loss due to both of these may not be recovered by exposure to oxygen. The width of Ca-induced gap states is broad (FWHM $\approx$ 1.0 eV). Therefore, the small difference in the ionization potential between 4PV and PPV (<0.5 eV) should not affect the quenching and recovery mechanisms in both materials. Preliminary work on Alq_3 have also exhibited metal induced PL quenching.

However, more work needs to be done before the mechanisms responsible for this quenching in Alq3 can be explained. Investigations are currently underway to characterize it.

SUMMARY

In summary, we have shown that the very act of depositing Ca, Ag, and Al on 4PV greatly diminishes the PL. Excitons will suffer non-radiative decay if created within the Ca atoms quenching radius. The importance of this finding is clear in light of reports that the recombination occurs near the metal cathode for hole conducting organic materials such as 4PV (Ref. 17, 18). Mechanisms which may be responsible for the PL intensity drop have been discussed. We have also presented strong evidence that the formation and removal of gap states in the Ca/4PV interface may be responsible for the quenching and recovery of its PL. From the PL intensity variation on cumulative Ca deposition/oxidation cycles, it was estimated that approximately 30 Å of oxidized Ca layer can be used as a protective layer against PL quenching due to fresh Ca deposition. This work improves our understanding of the role of interfaces in device performance, and has obvious ramifications on the LED applications.

ACKNOWLEDGEMENTS

This work was supported in part by the National Science Foundation under Grant No. DMR-9612370 and by DARPA DAAL 0196K0086. We would like to thank T. Wehrmeister and K. Müllen for providing the 4PV used.

REFERENCES

(1) H. Antoniadis, B. R. Hsieh, M. A. Abkowitz, *et al.*, *Appl. Phys. Lett.* **62**, 3167 (1993).
(2) H. Antoniadis, M. A. Abkowitz, M. Stolka, *et al.*, *Synth. Met.* **62**, 265 (1994).
(3) D. D. C. Bradley, *Synth. Met.* **54**, 401 (1993).
(4) G. Horowitz, *Advance Materials* **2**, 287 (1990).
(5) D. Braun and A. J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).
(6) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
(7) J. Kido, M. Kimura, and K. Nagai, *Science* **267**, 1332 (1995).
(8) C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
(9) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, *et al.*, *Nature* **347**, 539 (1990).
(10) E. Ettedgui, H. Razafitrimo, Y. Gao, *et al.*, *Appl. Phys. Lett.* **67**, 2705 (1995).

(11) E. Ettedgui, H. Razafitrimo, Y. Gao, *et al.*, *Phys. Rev. Lett.* **76**, 299 (1996).

(12) H. Razafitrimo, E. Ettedgui, L.-H. Guo, *et al.*, *Appl. Phys. Lett.* **67**, 2621 (1995).

(13) D. D. C. Bradley, *Advance Materials* **4**, 756 (1992).

(14) A. R. Brown, D. D. C. Bradley, J. H. Burroughes, *et al.*, *Appl. Phys. Lett.* **61**, 2793 (1992).

(15) N. C. Greenham, R. H. Friend, A. R. Brown, *et al.*, *Proceedings of the SPIE* **1910**, 84 (1994).

(16) I. D. Parker, *J. Appl. Phys.* **75**, 1656 (1994).

(17) H. Antoniadis, B. R. Hsieh, M. A. Abkowitz, *et al.*, *Mol. Cryst. Liq. Cryst.* **256**, 381 (1994).

(18) U. Lemmer, S. Karg, M. Scheidler, *et al.*, *Synth. Met.* **67**, 169 (1994).

(19) V. Choong, Y. Park, Y. Gao, *et al.*, *Appl. Phys. Lett.* **69**, 1492 (1996).

(20) S. A. Brazovskii and N. N. Kirova, *Synth. Met.* **55-57**, 4385 (1993).

(21) P. S. Davids, A. Saxena, and D. L. Smith, *J. Appl. Phys.* **78**, 4244 (1995).

(22) M. Fahlman, D. Beljonne, M. Lögdlund, *et al.*, *Chem. Phys. Lett.* **214**, 327 (1993).

(23) G. Iucci, K. Xing, M. Lögdlund, *et al.*, *Chem. Phys. Lett.* **244**, 139 (1995).

(24) D. Steinmüller, M. G. Ramsey, and F. P. Netzer, *Phys. Rev. B* **47**, 13323 (1993).

(25) Y. Park, E. Ettedgui, Y. Gao, *et al.*, *Polymer Preprints* **36**, 382 (1995).

(26) Y. Park, V. Choong, E. Ettedgui, *et al.*, *Appl. Phys. Lett.* **69**, 1080 (1996).

(27) R. Schenk, M. Ehrenfreund, W. Huber, *et al.*, *J. Chem. Soc., Chem. Commun.* **22**, 1673 (1990).

(28) R. Schenk, H. Gregorius, K. Meerholz, *et al.*, *J. Am. Chem. Soc.* **113**, 2634 (1991).

(29) H. S. Woo, O. Lhost, S. C. Graham, *et al.*, *Synth. Met.* **59**, 13 (1993).

(30) M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, *et al.*, *Phys. Rev. Lett.* **73**, 744 (1994).

(31) M. J. Rice and Y. N. Garstein, *Phys. Rev. B* **53**, 10764 (1996).

(32) W. R. Salaneck and J. L. Brédas, *Advance Materials* **8**, 48 (1996).

(33) C. Kittel, *Introduction to Solid State Physics* (John Wiley, N. Y., 1986).

(34) D. J. Griffiths, *Introduction to Electrodynamics* (Prentice Hall, N. J., 1989).

(35) P. Dannetun, M. Fahlman, C. Fauquet, *et al.*, *Synth. Met.* **67**, 133 (1994).

(36) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, *et al.*, *Science* **258**, 1474 (1992).

(37) S. Morita, A. A. Zakhidov, and K. Yoshino, *Solid State Comm.* **82**, 249 (1992).

(38) K. Yoshino, X. H. Yin, K. Muro, *et al.*, *Japanese Journal of Applied Physics* **32**, L359 (1993).

(39) H. Antoniadis and B. R. Hsieh, *Chem. Phys. Lett.* **238**, 301 (1995).

(40) P. Bröms, J. Birgersson, N. Johansson, *et al.*, *Synth. Met.* **74**, 179 (1995).

(41) Y.-E. Kim, H. Park, and J.-J. Kim, *Appl. Phys. Lett.* **69**, 599 (1996).

(42) A. C. Fou, O. Onitsuka, M. Ferreira, *et al.*, *J. Appl. Phys.* **79**, 7501 (1996).