Photo-induced charge and luminescence measurements of evaporated ZnS:Mn alternating-current thin-film electroluminescent devices

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Abstract — Photo-induced charge (PIQ) and photo-induced luminescence (PIL) measurements are employed for the characterization of evaporated ZnS:Mn alternating-current thin-film-electroluminescent (ACTFEL) devices. PIQ and PIL measurements involve monitoring the charge and luminescence associated with the transport of UV-excited electrons or holes under the application of a constant applied voltage. The experiment is accomplished using a short UV laser pulse to create carriers near the upper phosphor/insulator interface while maintaining a constant voltage across the ACTFEL device in order to set the phosphor field. By changing the polarity of the applied voltage pulse, either electron or hole transport may be studied. PIL thresholds indicate that the critical field for electron-initiated electroluminescence in ZnS is ~1.04 MV/cm. PIQ trends indicate that electron transport is significantly more efficient than hole transport due to hole trapping in the ZnS. Hole trapping is characterized by a drift length of ~180 ± 70 nm, a hole lifetime of ~2 ps, and a capture cross-section of ~7 × 10⁻¹³ cm². A capture cross-section of this magnitude corresponds to hole trapping by negatively charged acceptor-like trap. It is speculated that this hole trap is a zinc vacancy complex.

Keywords — Electroluminescence, electro-optic characterization, TFEL phosphors, TFEL devices, photoluminescence, charge transfer.

1 Introduction

Photo-induced transferred charge (PIQ) and photo-induced luminescence (PIL) measurements have been employed for several groups for the characterization of alternating-current thin-film-electroluminescent (ACTFEL) devices.1-7 PIQ and PIL experiments involve the creation of electron-hole pairs (generated by a short ultraviolet laser pulse) in the phosphor near one of the phosphor/insulator interfaces, transport of this photo-induced charge across the phosphor (aided by the application of a DC voltage across the ACTFEL stack), and measurement of the charge transferred across the phosphor layer or the luminescence emitted from the phosphor layer, respectively, as a function of the magnitude of the applied DC voltage.

PIQ/PIL measurements were originally developed by Corlatan et al. who analyzed evaporated ZnS:Mn ACTFEL devices with probe layers in which only certain regions of the phosphor were Mn-doped.1,2 One of the advantages of PIQ/PIL experiments is that electron and hole transport may be studied independently by simply changing the polarity of the DC bias. Corlatan et al. concluded that in ZnS:Mn ACTFEL devices hole transport may give rise to impact-excitation-induced electroluminescence, holes are approximately half as efficient as electrons in contributing to the transferred charge, and the efficiency of transport (where efficiency is defined as PIL divided by PIQ) is significantly greater for holes than electrons. Their conclusion that the photo-induced hole efficiency is greater than the photo-induced electron efficiency was very surprising to them; they interpreted this result as arising from differences in the electric-field profile in the phosphor for the cases of hole and electron transport.

The Heinrich-Hertz Institute (HHI) group has employed PIQ/PIL measurements for the characterization of transport in multi-source-deposited SrS:Ce ACTFEL devices.3-7 They find no evidence for hole transport in their devices. Thus, carrier transport in SrS:Ce ACTFEL devices is dominated by electrons. PIQ/PIL trends point to the important role of dynamic space charge in determining the behavior of SrS:Ce devices. Furthermore, PIQ/PIL measurements provide evidence for electron multiplication in SrS at fields significantly below that of the normal ACTFEL threshold. This electron multiplication is attributed to defect ionization.

The purpose of the work described herein is to present a PIQ/PIL study of commercial-quality evaporated ZnS:Mn ACTFEL devices of variable phosphor thickness. The trends found in this study are consistent with the work of Corlatan et al.1,2 In agreement with Corlatan et al. we find the efficiency of hole transport to be greater than that of electron transport. In contrast to Corlatan et al., we attribute this trend to hole trapping which modifies the

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Revised version of a paper presented at the Third International Conference on the Science and Technology of Display Phosphors, Nov. 3-5, 1997, Huntington Beach, CA.

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Journal of the SID Supplement-1, 2000 51
electric field profile in the phosphor. Moreover, the data which appears to be due to hole transport is attributed to electron injection from the opposite phosphor-insulator interface.

A word of caution is required when comparing PIQ/PIL data from different groups. Of the three groups reporting PIQ/PIL results, all perform these experiments in a different manner. Our procedure is very close, yet not identical, to that of Corlatan et al. but is very different than that of the HHI group. Differences between PIQ/PIL procedures are discussed in the experimental procedure section.

2 Experimental procedure

The samples used in this study are fabricated at Planar America and consist of a standard ACT FEL structure with SiON top and bottom insulators, evaporated ZnS:Mn as the phosphor layer, an indium-tin oxide bottom contact, and aluminum top contact. The top and bottom insulator thicknesses are approximately 110 nm and 180 nm, respectively, for all three of the ACTFEL devices used in this study. Phosphor thicknesses are 300, 700, and 950 nm. For PIQ/PIL experiments, an ~15-nm-thick semi-transparent layer of aluminum is thermally evaporated onto the sample so that a small portion of this layer overlaps neighboring thick aluminum dots, but the majority of the thin contact covers the uncontacted ACTFEL stack. The purpose of this semi-transparent aluminum layer is to allow ultraviolet laser radiation to pass through the thin contact, creating electron-hole pairs in the phosphor, and yet to allow carriers to be collected via the semi-transparent contact.

The theoretical basis of PIQ/PIL measurements is that electron-hole pairs are generated within ~40-60 nm of the nearest phosphor surface by an ultraviolet laser pulse. When the aluminum contact is negatively biased, photo-induced electrons are transported across the phosphor, while holes remain close to the phosphor/insulator interface at which they are created. The PIQ signal is a function of the number of photo-generated electrons and the distance that each electron travels. The PIL signal is the measured luminescence that arises from impact excitation of Mn atoms as these photo-induced electrons transit the phosphor. When the aluminum contact is positively biased, the holes traverse the phosphor, giving rise to PIQ and PIL, and electrons remain close to the phosphor/insulator interface at which they are created.

The PIQ/PIL experimental set-up is shown in Fig. 1. The ultraviolet radiation is generated by a nitrogen laser at a wavelength of 337 nm pumping a dye laser tuned to 500 nm, which then passes through a doubling crystal to create 250 nm wavelength pulses of 2-3 ns duration. Since the band gap of ZnS is 3.7 eV (330 nm), this photon energy is sufficiently large to create electron-hole pairs by band-to-band generation. The DC voltage applied to the ACTFEL device is generated by an arbitrary-waveform generator (Wavetek model 395) and amplified by a high-voltage amplifier. The PIQ signal is measured by means of a 100-pF sense capacitor in series with the ACTFEL device via a digitizing oscilloscope (Tektronix model TDS 420A). The PIL signal is measured by placing a fiber-optic bundle at the edge of the glass substrate and passing the collected light through a monochromator (Jarrell-Ash model 82-140) to a photomultiplier tube (Hamamatsu model R928) which is then monitored by the digital oscilloscope.

In a PIQ/PIL experiment, the PIQ and PIL signals are measured as a function of the magnitude of the applied voltage across the ACTFEL device. In order to obtain more meaningful PIQ/PIL data, we found it desirable to optically reset the phosphor field to a flat-band condition between each voltage pulse. To accomplish this, a xenon lamp is used to apply an optical reset pulse between each DC voltage/laser pulse.

By exposing the phosphor to broad-band radiation any space charge trapped within the device can theoretically be eliminated. The use of an optical reset pulse to create a reproducible flat-band situation was first investigated by Corlatan et al.2

A timing diagram for the PIQ/PIL measurements is shown in Fig. 2. The ACTFEL device is first reset with a 10-s optical reset. Next, a positive voltage pulse with 5-µs rise and fall times and a 100-µs plateau is applied. 30 µs after the beginning of the electrical pulse, a 3-ns laser pulse is applied. The maximum charge induced on the sense capacitor and the integrated area of the PMT signal (the total light output) generated by the device for that pulse are stored via computer acquisition. The ACTFEL device is then optically reset again and a negative voltage pulse is applied. Once

FIGURE 1 — PIQ/PIL measurement set up. Dashed lines denote measurement of the voltage across the sense capacitor and the voltage from the PMT.
again, the maximum charge induced on the sense capacitor and the light produced are stored.

For each maximum applied voltage, two sets of PIQ/PIL data are acquired. The first set of data is obtained when the voltage pulse is applied in the absence of a laser pulse (Fig. 2a), while the second set is obtained when both the voltage pulse and the laser pulse are applied (Fig. 2b). These two sets of data are then subtracted from one another in order to isolate the photo-induced PIQ and PIL signals. After acquisition of four sets of data, the two sets described above for both positive and negative applied voltages, the maximum applied voltage of the pulse is increased and the process is repeated. PIQ and PIL data are taken in 5 V steps from 0 V to 20-40 V above threshold for three different ZnS:Mn phosphor thicknesses. Additionally, a PIQ/PIL efficiency is determined by dividing the PIL by the PIQ and is a measure of the efficiency of the photo-induced transferred charge (electrons or holes) at generating luminescence.

Our method for accomplishing PIQ/PIL measurements differs from that of the other groups performing PIQ/PIL measurements. In particular, Corlatan et al. do not perform a difference curve analysis of their data by subtracting a data set in which the laser is not applied, as described above and shown in Fig. 2(c). Therefore, their PIQ/PIL data includes the effects of normal electroluminescence, while our method attempts to isolate the response to only photo-injected carriers. The work performed by Corlatan et al. also differs from ours in that their samples possess probe layers of doped phosphor, while our samples are uniformly doped. In contrast, the PIQ/PIL measurements performed by the HHI group differ significantly from those of the other two groups in that no optical reset pulse is used and the devices are driven continuously with an electrical pulse. In this method, each set of data is obtained by driving the device electrically with 100 pulses at a given voltage, followed by a measuring pulse which is applied at the same time as the laser pulse. This allows the device to reach steady-state before application of the laser pulse. However, the steady-state condition is different for each voltage, whereas an optical reset pulse allows one to start from the same initial condition before each measuring pulse.

3 Experimental results and discussion

The primary experimental results of this study are presented in Figs. 3 and 4 in which PIL and PIQ are plotted as a function of the maximum voltage applied to the ACTFEL device with phosphor thickness of 950 nm. The PIL and PIQ curves for the ACTFEL devices with phosphor thicknesses of 700 and 300 nm exhibit trends similar to those shown in Figs. 3 and 4. Therefore, PIL and PIQ curves for the ACTFEL devices with phosphor thicknesses of 700 and 300 nm are not shown in this paper.
The PIL results are discussed first. A definite PIL threshold is evident for all three ACTFEL devices measured, as seen in Fig. 3. This PIL threshold corresponds to the phosphor field at which the photo-injected carriers are hot enough to excite luminescent impurities. All of the data sets have a baseline offset which is due to the photo-luminescence (PL) response of the device. The PL response is the light produced by the laser exciting the phosphor in the absence of an electric field-induced response. Therefore, the PL offset baseline can be taken as the origin when calculating the threshold field. The PIL phosphor threshold field is calculated from

\[ F_{th} = \frac{C_i V_{th}}{d_p (C_i + C_p)} \]  

(1)

where \( V_{th} \) is the voltage intercept of the PIL with the PL offset baseline (Fig. 3), \( d_p \) is the phosphor thickness, and \( C_i \) and \( C_p \) are the phosphor and insulator capacitances, respectively. The calculated phosphor threshold fields are 1.05 MV/cm for the 950-nm sample, 1.04 MV/cm for the 700-nm sample, and 1.03 MV/cm for the 300-nm sample. A PIL threshold for the holes as is also observed; but it is our contention that this threshold actually arises from injection from the opposite interface, as discussed below. The reason that the PIL reaches a peak and then decreases is believed to be an artifact arising from the difference curve analysis; the photo-injected carriers contribute a small fraction of the light at higher fields where electroluminescence dominates. Therefore, the data points for voltages greater than that of the peak voltage are not meaningful and the PIL peak is not significant.

The measured PIL threshold of ~1.04 MV/cm is somewhat larger than the 0.7 MV/cm threshold field for impact excitation calculated via a full-band Monte Carlo simulation, but it is in excellent agreement with the band-to-band impact ionization threshold of 1 MV/cm from the Monte Carlo calculation. A comparison of the experimental PIL results and the full-band Monte Carlo simulation suggests that the PIL threshold may be associated with the onset of electron multiplication due to band-to-band impact ionization. This suggests that the PIL is not due to only the photo-injected carriers, but is also due to carriers created by impact ionization. Alternatively, it is possible that the experimentally deduced 104 MV/cm PIL threshold corresponds to the onset of Mn impact excitation and that the disagreement between the measured and Monte Carlo simulated impact excitation thresholds arises because of uncertainties in the Monte Carlo simulation parameters. Although this second interpretation is possible, we prefer to attribute the measured PIL threshold to the band-to-band impact ionization threshold for two reasons. First, in Fig. 3 we see no evidence for a second threshold corresponding to the onset of band-to-band impact ionization. Second, we believe that an important condition for efficient ACTFEL operation is that the threshold field for band-to-band impact ionization be less than or equal to the threshold for impact excitation; in an ACTFEL device, this condition leads to electron multiplication of electrons sourced from interface states.

The PIQ curves for the ACTFEL device with a phosphor thickness of 950 nm (Fig. 4) clearly show a region below ~125 V where the holes are not as efficient at traversing the phosphor. In contrast, above ~125 V the electrons and holes have approximately the same transport efficiency, since the slope of the PIQ curve above 125 V is the same for both electrons and holes (i.e., the slope of a PIQ curve can be viewed as a transport efficiency.) ACTFEL devices with phosphor thicknesses of 700 and 300 nm exhibit trends similar to those shown in Fig. 4 in which the hole PIQ efficiency distinctly increases above a certain applied voltage. The voltage at which the PIQ efficiency increases is ~75 and ~50 V for ACTFEL devices with 700 and 300 nm thick phosphor layers, respectively. The voltage at which the transport efficiency changes corresponds to an internal phosphor field of ~0.8 MV/cm for all three ACTFEL devices. The value of 0.8 MV/cm obtained from the PIQ experiment is an average field across the phosphor; the cathode field is significantly larger if space charge is present, as discussed below.

We interpret these PIQ results to suggest hole trapping in the phosphor for lower fields; the transport efficiency of holes is less than that of the electrons since a significant fraction of the photo-injected holes are trapped in the phosphor, while the electrons transit the phosphor layer with very little trapping. This interpretation of the PIQ data in terms of hole trapping is consistent with the analysis of Corlatan et al. As mentioned previously, the hole transport efficiency seems to be approximately equal to the electron transport efficiency above a certain maximum applied voltage (~125 V, ~75 V, and ~50 V for phosphor thicknesses of 950 nm, 700 nm, and 300 nm, respectively). Corlatan et al. interpreted this as evidence that Mn impact excitation can occur via hot holes. In contrast, we offer an alternative explanation of the experimental trends.
It is more likely that the apparent hole transport is actually due to electron transport in which electrons are injected from the opposite interface via back-injection, as illustrated in Fig. 5. As holes are trapped in the phosphor, the energy bands are bent, causing an increase in the backside cathode field which effectively lowers the tunnel injection barrier, as indicated in Fig. 5. Thus, the apparent increase in the hole PIQ efficiency at voltages greater than ~125 V and ~75 V for ACTFEL devices with phosphor thicknesses of 950 and 700 nm, respectively, would actually correspond to an onset of electron injection from the backside cathode interface. It is impossible to distinguish holes moving away from the top interface from electrons moving towards it. However, if back injection of electrons does indeed occur, we would expect to see a shift in the PIQ threshold towards higher voltages with lower laser intensity, due to less hole trapping and a concomitant reduction in the cathode field enhancement. This hypothesis is tested by acquiring a second set of PIQ data using a laser intensity ~100 times less than that used to acquire the first set of data. For ACTFEL devices with phosphor thickness of 950 and 700 nm, a shift in the PIQ curve toward higher voltages is observed, consistent with our hypothesis that the apparent increase in the hole PIQ efficiency actually arises from the transport of electrons injected from the opposite interface. A lower laser intensity PIQ curve for the ACTFEL device with a phosphor thickness of 950 nm is shown in Fig. 6. Note that the PIQ hole efficiency for this curve increases above a voltage of ~160 V instead of ~125 V as shown in Fig. 3. Similar trends are seen for the ACTFEL device with phosphor thickness of 700 nm where the lower intensity PIQ hole transition voltage is ~100 V. The lower laser intensity PIQ curve for the ACTFEL device with phosphor thickness of 300 nm does not exhibit a strong shift in PIQ hole transition voltage.

If hole trapping and backside electron injection is invoked to explain the observed apparent increase in the hole PIQ efficiency for phosphor fields greater than ~0.8 MV/cm, it is possible to estimate the trapped hole concentration, $\rho$. This is accomplished by assuming a cathode field of 2.2 MV/cm$^1$ and using

$$\rho = \left[ \frac{\rho_{\text{cathode}} - F_{\text{measured}}}{p} \right]^{2/2} d_p,$$

which implicitly assumes a uniform distribution of trapped holes. Use of Eq. (2) yields an estimated $\rho$ of 1-5 $\times$ 10$^{17}$ cm$^{-3}$ for both ACTFEL devices tested. These estimates do not seem unreasonable since they are somewhat larger than the 7 $\times$ 10$^{16}$ cm$^{-3}$ estimates of the static space-charge density for evaporated ZnS:Mn ACTFEL devices.$^9,10$

A drift length for holes may be estimated from the PIQ measurement. If the electrons are assumed to transit completely across the phosphor, then at a given voltage, the ratio of the hole PIQ to the electron PIQ multiplied by the phosphor thickness of the device should yield an estimate of the average distance that holes travel prior to being trapped (i.e. the drift length) at that applied voltage. Figure 7 is a plot of the drift length as a function of the internal phosphor field. Note that the lowest field points plotted in Fig. 7 are not reliable because of the PIQ uncertainties. Also, the upward trend in the hole drift length of Fig. 7 for phosphor fields greater than ~0.8 MV/cm arises from the onset of backside electron injection, not from an enhancement in the hole drift length. Thus, taking the relatively constant, low-field portion of Fig. 7 as a measure of the drift length, the hole drift length is estimated to be 180 ± 70 nm. If holes are assumed to travel at a saturated drift velocity of ~10$^7$ cm/s, then the drift distance can be used to deduce an average hole lifetime of ~2 ps. Furthermore, if the hole trap density is assumed to be 7 $\times$ 10$^{16}$ cm$^{-3}$, the hole trap capture cross section can be estimated from

![Graph of Photo-Induced Charge vs. Voltage](image1.png)

**FIGURE 6** — Lower-laser-intensity PIQ curve for evaporated ZnS:Mn ACTFEL device with a phosphor thickness of 950 nm. Filled (empty) circles correspond to the electron (hole) responses.

![Graph of Drift Length vs. Average Phosphor Field](image2.png)

**FIGURE 7** — Hole drift length versus average phosphor field for evaporated ZnS:Mn ACTFEL devices with phosphor thickness of (a) 950 nm, (b) 700 nm, (c) 300 nm. The hole drift length is estimated from the relatively constant, low-field portions of the curves.
where $\tau$ is the hole lifetime, $v_{sat}$ is the saturated drift velocity, and $N_t$ is the trap density. Equation (3) yields an estimated capture cross-section of $\sim 7 \times 10^{-13}$ cm$^2$. This is a relatively large capture cross-section. Capture cross-sections of this magnitude correspond to a coulombically attractive interaction between a trap and the carrier to be trapped. Thus, the large magnitude of this capture cross-section suggests that the trap is negatively charged prior to hole capture. We speculate that this hole trap is a zinc vacancy or, more likely, a zinc vacancy complex, since a zinc vacancy is a double acceptor. More work is required to conclusively identify the physical nature of this hole trap.

Returning to the PIQ curve shown in Fig. 4, it is puzzling that the electron PIQ signal increases monotonically over the entire range of the maximum applied voltage. Since the strength of the PIQ signal is determined by the integral of the product of the number of carriers transported times the distance that they travel before being trapped, the monotonous nature of the electron PIQ signal appears to suggest that either (i) more carriers are transported at larger applied voltages, or (ii) carriers travel further at larger maximum applied voltages before being trapped. We prefer to invoke possibility (i) to explain the electron PIQ trend shown in Fig. 4 and offer two possible reasons for carrier enhancement. First, at the higher phosphor fields concomitant with a larger applied voltage there may be an increase in the number of transported carriers due to electron multiplication of the photo-induced carriers as they transit the phosphor; such electron multiplication could occur via trap-to-band impact ionization, for example. Second, given the large number of photons injected into the phosphor, it is likely that electron-hole pair recombinations of photo-injected carriers in the region near the incident interface will be very high in the absence of an applied field. When an external field is applied, more carriers will be extracted from the recombination region before they have a chance to recombine, leading to the lack of saturation of the PIQ curves. If this second mechanism is operative, the PIQ efficiency would be due to the extrication efficiency of the photo-injected carriers as well as to the transport efficiency.

Finally, we turn to the quantum efficiency, which is defined as the ratio of the PIL to the PIQ. Although the quantum efficiency data is not plotted, such curves may be interpreted as indicating that electrons and holes are equally efficient in exciting luminescent impurities, as reported by Corlatan quantum efficiency data is not plotted, such curves may be. If this second mechanism is operative, the PIQ efficiency would be due to the extraction efficiency of the phosphor; such electron multiplication could occur via trap-to-band impact ionization, for example. Second, given the large number of photons injected into the phosphor, it is likely that electron-hole pair recombinations of photo-injected carriers in the region near the incident interface will be very high in the absence of an applied field. When an external field is applied, more carriers will be extracted from the recombination region before they have a chance to recombine, leading to the lack of saturation of the PIQ curves. If this second mechanism is operative, the PIQ efficiency would be due to the extrication efficiency of the photo-injected carriers as well as to the transport efficiency.

Finally, we turn to the quantum efficiency, which is defined as the ratio of the PIL to the PIQ. Although the quantum efficiency data is not plotted, such curves may be interpreted as indicating that electrons and holes are equally efficient in exciting luminescent impurities, as reported by Corlatan et al. A more likely explanation, as mentioned previously, is that the apparent hole transport trends are actually due to electron injection from the opposite interface; this process is more efficient because hole trapping significantly perturbs the electric field profile due to the formation of positive space charge. This interpretation is in contrast with that of Corlatan et al. who conclude that the hole-initiated PIQ/PIL data is due to holes, and that hole-initiated Mn excitation is more efficient than electron-initiated Mn excitation.

4 Conclusions

Photo-induced charge (PIQ) and photo-induced luminescence (PIL) measurements of evaporated ZnS:Mn ACTFEL devices with variable phosphor thicknesses provide information related to the transport of electrons and holes in the ZnS phosphor. The PIL threshold field for electron transport is estimated to be $\sim 1.04$ MV/cm, in excellent agreement with Monte Carlo simulation of high-field transport in ZnS. However, it is possible that this threshold arises from the electron-induced impact ionization of Mn. The hole PIL threshold is found to be an artifact due to electron injection from the interface opposite from which the photo-induced holes are created. Hole PIQ curve trends are dominated by hole trapping. Hole trapping is characterized by a drift length of $\sim 180 \pm 70$ nm, a hole lifetime of $\sim 2$ ps, and a trap capture cross-section of $\sim 7 \times 10^{-13}$ cm$^2$. This is a large capture cross section, corresponding to a negatively charged deep level trap whose charge state leads to very efficient hole capture due to the attractive coulombic interaction between the trap and the hole. We speculate that this hole trap is most likely a defect complex involving a zinc vacancy.

Acknowledgements

This work was supported by the U.S. Army Research Office under Contract No. DAAH04-94-G-0324 and by the Defense Advanced Research Projects Agency under the Phosphor Technology Center of Excellence, Grant No. MDA 972-93-1-0030.

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