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Electroluminescence in Amorphous Pyrazoline Films Under DC Fields

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We have investigated the electroluminescence, EL, behavior in amorphous films of a pyrazoline derivative under dc fields. The current vs. voltage characteristics indicated a space charge limited current behavior with traps distributed exponentially within the forbidden energy gap. EL was detected in the current range of double carrier injection which occurred after all traps in the sample were filled up. Spectral studies showed that the light emission zone was localized around the cathode side of the pyrazoline film. The brightness, measured as a function of current, indicated the EL in the lower current density range to be dominated by delayed luminescence.

Keywords: delayed luminescence, double carrier injection.

INTRODUCTION

Electroluminescence (EL) is one of the well-known phenomena which can be readily applied to the design of display devices. However, while studies on thin film EL displays fabricated from inorganic materials have been carried out extensively, interests on EL in organic materials have been rather limited except for some work in organic single crystals of aromatic compounds having condensed rings.[1] The electroluminescence in organic single crystals has generally been attributed to radiative decay of singlet excitons that are produced by recombination of holes and electrons.[2,3]

Recently, several papers on EL in organic thin films have been published which has a potential of being used in large area display

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devices. These films are made from polymer films,[4] or vacuum-deposited films,[5] or Langmuir-Blodgett films.[6,7] As part of this effort in thin organic films, we have reported the first observation of ac-field induced electroluminescence in amorphous films of a pyrazoline derivative which were sandwiched between indium-tin-oxide (ITO) and aluminum electrodes.[8] The pyrazoline compounds are particularly attractive for use in EL devices because they can be easily fabricated into stable amorphous films. It is generally thought that amorphous films have higher dielectric breakdown strengths than their polycrystalline counterparts because they have fewer defects such as grain boundaries and/or spherulite centers.

In this paper, we report the EL behavior of the pyrazoline compounds under dc-fields and discuss the possible mechanisms on the basis of current-voltage characteristics and EL spectra.

EXPERIMENTAL

The material used in this study was 1-phenyl-3-(*p*-diethyl aminostyril)-5-(*p*-diethyl aminophenyl)-2-pyrazoline, denoted henceforth as Py-1.[9] The fabrication procedure for the sandwich-type EL cells was similar to that described before.[8] Semitransparent Al electrode was used as the cathode while Au, ITO and CuI semitransparent electrodes were employed as the anode. The vacuum pressure during deposition was about 10^{-5} torr and the electrode area was 0.5 cm^2.

Current densities were measured using a Keithly 614 electrometer. EL spectra were acquired by means of an Oriel monochrometer (Model 77250) and a Hamamatsu photon counter (Model C767) connected to a photomultiplier (R464) of the same maker. All electrical measurements were carried out in helium ambient at room temperature.

RESULTS AND DISCUSSION

1. Voltage-dependence of current density

The EL cells showed a good rectification effect in the current (I)-voltage (V) measurements. A typical result of the Au/Py-1/Al cell is shown in Figure 1. Since the cell shows an ohmic behavior in the lower voltage region when it is sandwiched with gold electrodes on both faces (see Figure 2, curve b), it is suggested that the aluminum electrode with a low work function made a blocking contact against Py-1.

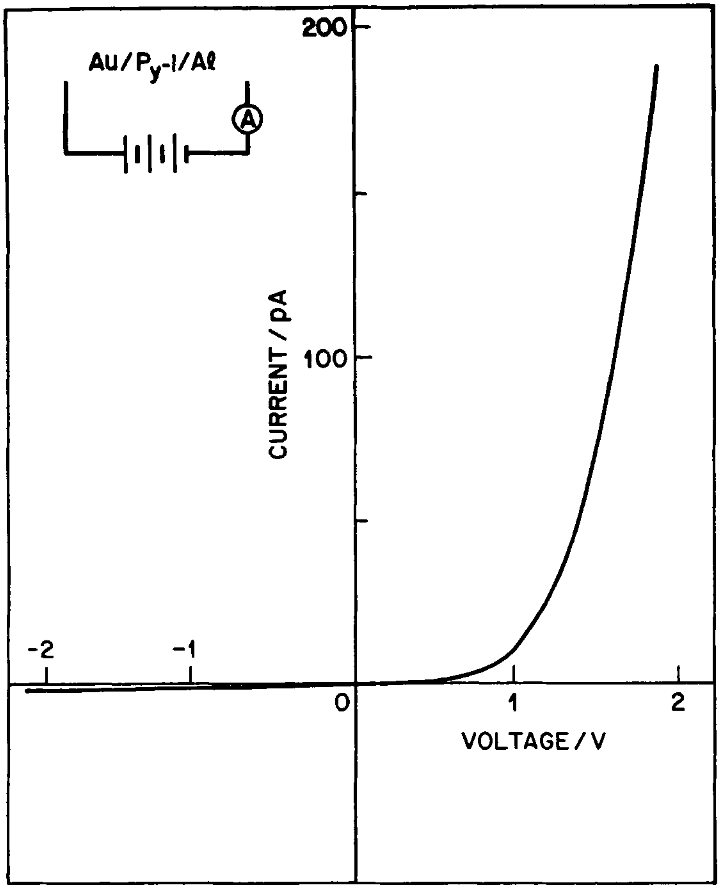

FIGURE 1 A plot of current vs. voltage for the Au/Py-1/Al cell.

The current density (J) vs. voltage characteristics for the Au/Py-1/Al cell in the forward direction are shown on a log-log plot in Figure 2, curve a. A power law dependence indicative of a typical space charge-limited-current (SCLC) behavior is observed. In the reverse direction, however, the current is much smaller and no SCLC is observed. A relationship of $J \propto V^7$ is obtained in the voltage range of 1.2 to 2.5 V. At higher voltages up to 20 V, the current is proportional to the square of voltage (i.e., $J \propto V^2$). These results are characteristic of an SCL current behavior with traps distributed exponentially within the forbidden energy gap.[10] For the sample under examination, the voltage when unfilled traps are completely filled, V_{TFL}, is equal to 2.5 V.

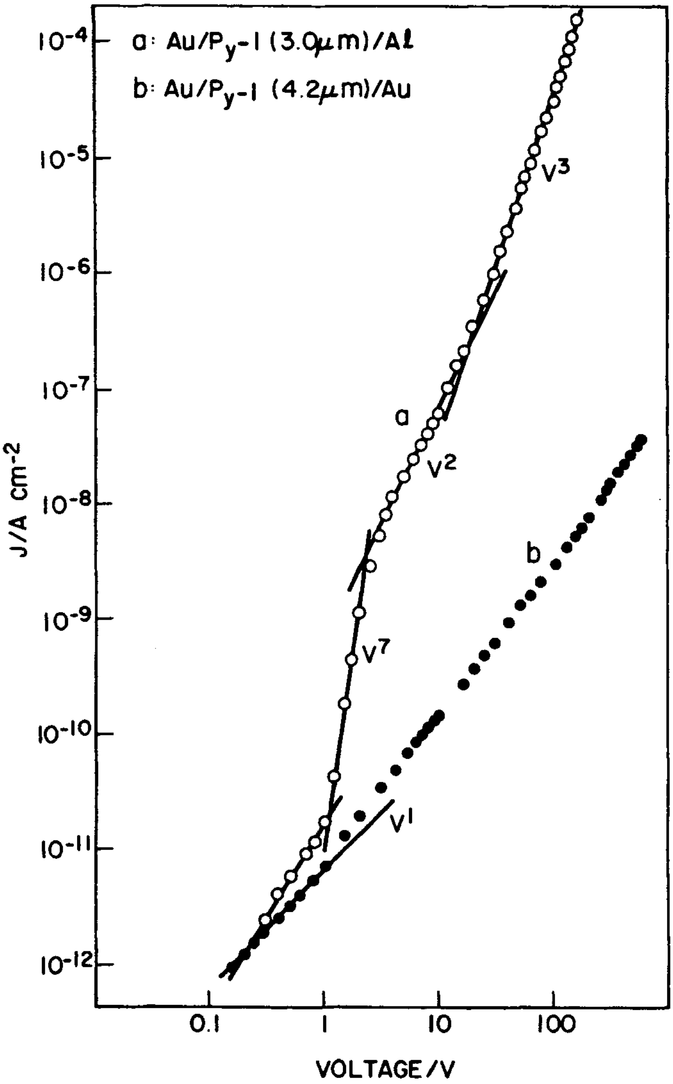

FIGURE 2 Log-log plots of *J-V* characteristics for the cells Au/Py-1/Al (curve a) and Au/Py-1/Au (curve b).

When all traps are filled up, a transition from the process of trapped SCL current to that of a trap-free SCL current takes place. Above V_{TFL}, the *J-V* behavior obeys the so-called Child's law, namely, $J \propto V^2$. In the case of Au/Py-1/Au cell, however, no SCL current is observed. This behavior, which is also observed in the Schottkey type diodes using organic semiconductors,[11,12] indicates that the interfacial region between Al and Py-1 affects the carrier injection.

At higher voltages, a cubic dependence of J on V is observed (see Figure 2, curve a) which suggests the phenomenon to be associated with double injection of carriers in accordance with the theory of Baron and Mayer.[13] In anthracene single crystals, it has been experimentally confirmed that the current behavior exhibits a cubic dependence in the case of double carrier injection.[14-16]

The CuI electrode is generally known to be a hole injection electrode.[1,17] The J-V behavior of the EL cell having a CuI electrode as the anode is shown in Figure 3, curve a. It can be seen that both curve a and curve b which corresponds to the J-V data of the ITO/Py-1/Al cell exhibit the same behavior that includes square and cube laws. The arrows in the figure indicate the threshold voltages at which the EL was detected. According to Kao and Huang,[18] a single carrier injection would change to a double carrier injection above a critical applied field because of the space charge built up near the blocking contact or neutral contact. If we accept this interpretation, the electroluminescence in amorphous Py-1 film is probably caused by double injection of carriers, a mechanism which is essentially the same as that for organic single crystals.

The threshold voltage depended on the materials used for anodes. For example, among the different combinations of electrode materials used in this experiment, the CuI/Py-1/Au cell exhibited the highest current density and a rather stable light emission.

Figure 4 shows the relationship between the brightness of EL and the current in the CuI/Py-1/Al cell. In the low current region, the brightness depended on the square of current; however, the exponent becomes progressively smaller with increasing current. The former result suggests that the brightness is dominated by the delayed EL in the low current region. The square dependence of brightness on current has also been observed in anthracene single crystals,[2] but our results are more definitive in that the square dependence extends over a wider range of current. The yield of light emission, estimated from the region (Figure 4) where the brightness is proportional to the current, is about 10^{-6} emitted photons per injected hole-electron pair if one assumes the numbers of injected electrons and holes to be the same.

2. Spectral characteristics

The corrected EL spectra of the CuI/Py-1/Al cell are shown in Figure 5 where the curve a was measured at the Al side of the cell and b

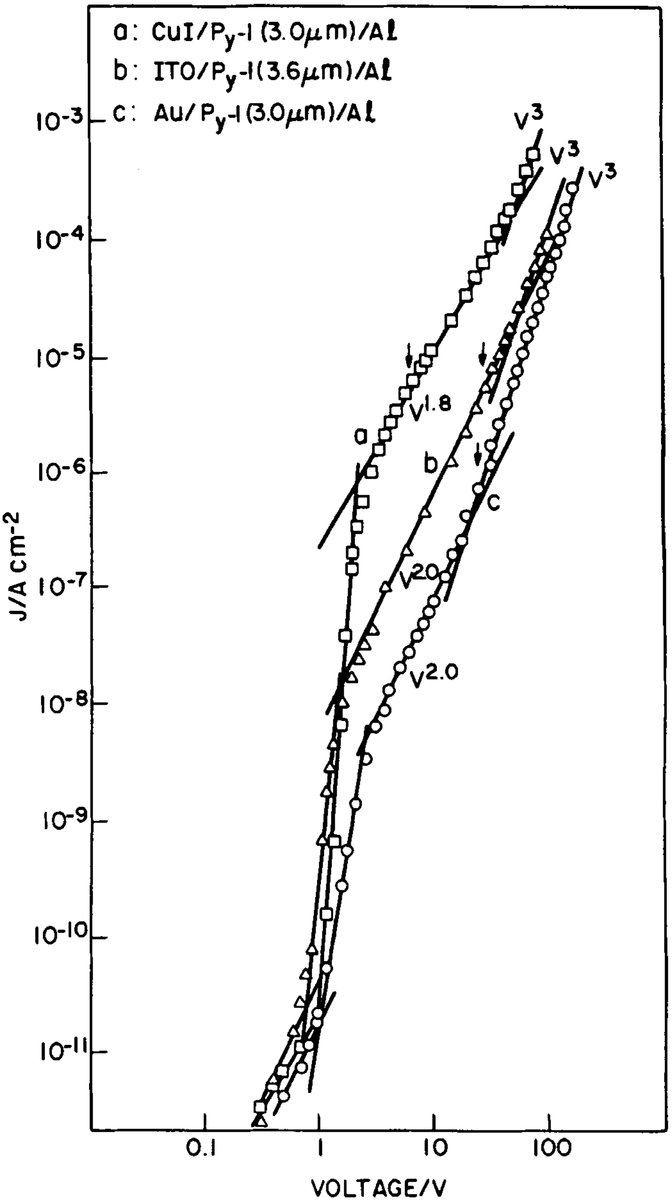

FIGURE 3 Log-log plots of *J-V* characteristics for the cells CuI/Py-1/Al (curve a), ITO/Py-1/Al (curve b) and Au/Py-1/Al (curve c). Arrows in the plots indicate the threshold voltage for electroluminescence.

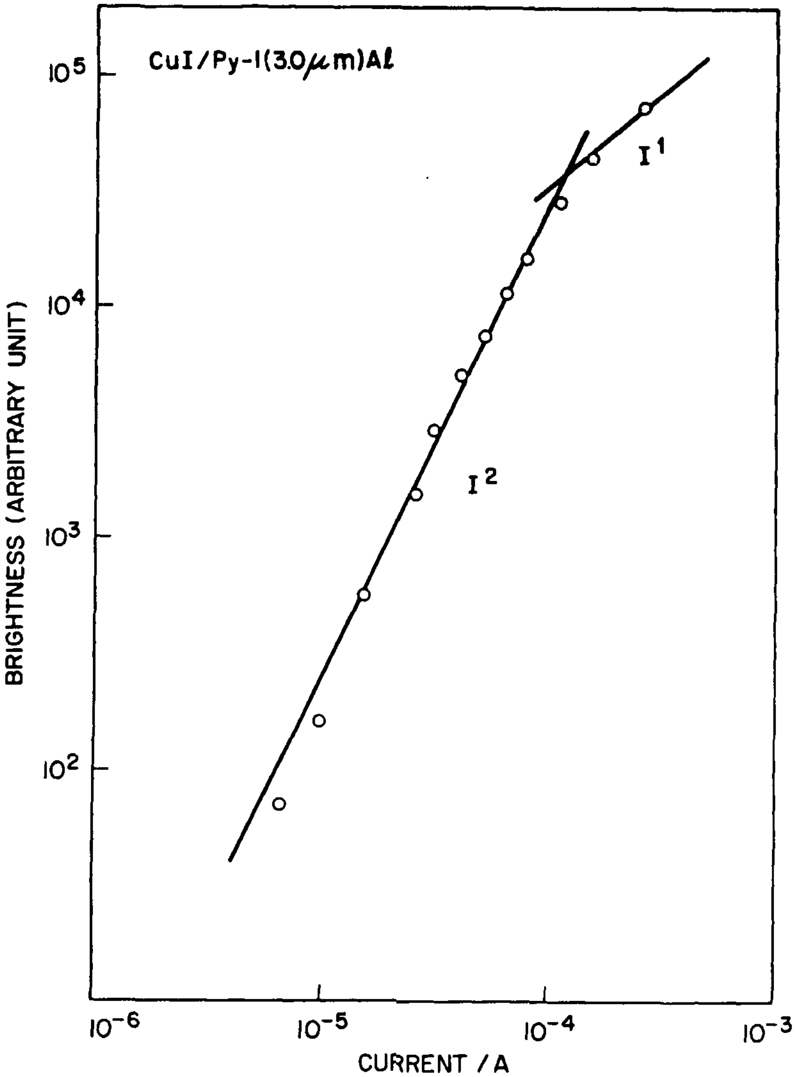

FIGURE 4 *Dependence of electroluminescence brightness on current in the* CuI/Py-1/Al cell.

was measured at the CuI side. Curve c is the absorption spectra of an amorphous Py-1 film. There are significant differences between curves a and b; in particular, the emission tail of curve a near 425–450 nm is not observed in curve b. This spectral behavior indicates that there is a distribution of emission zone in the direction of film

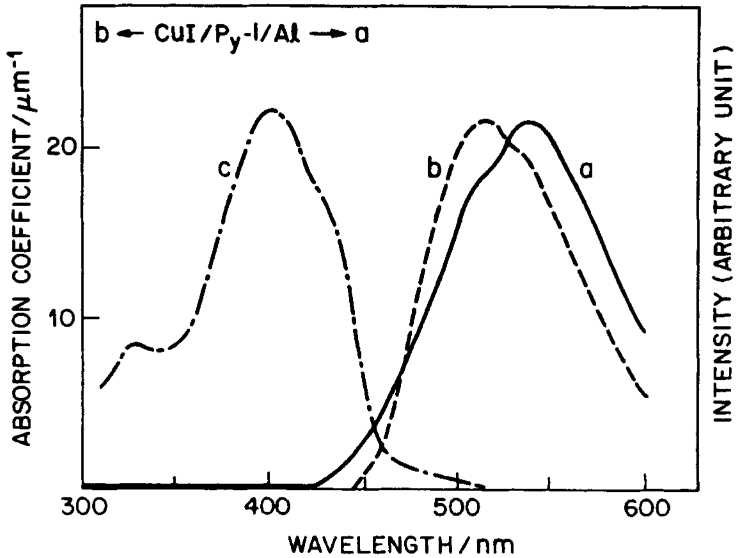

FIGURE 5 Corrected spectra of electroluminescence as observed from the cathode side (curve a) and the anode side (curve b), and the absorption coefficient of amorphous Py-1 film (curve c).

thickness. Since the absorption coefficient of Py-1 increases in the region 425–450 nm, the absence of an emission tail in curve b is probably caused by the self-reabsorption of pyrazoline molecules.

To confirm this, photoluminescence spectra of an amorphous Py-1 film excited at 400 nm were measured and the corrected fluorescence spectra are shown in Figure 6. As can be seen from the sketch in the inset, curve a was measured from the side facing the surface of incident beam and b from the opposite side. Since the excitation light (at 400 nm) is mostly absorbed at the film surface, the emission zone of fluorescence is localized near the surface region of the Py-1 film. It will be noted from Figure 6 that the shape of each spectral curve is quite similar to the corresponding curve in Figure 5. This result supports our suggestion that the light emission zone in the CuI/Py-1/Al cell is localized near the Al electrode side of the Py-1 film. This localization of emission zone appears to have been caused by the sharp difference in the carrier mobility between holes (μ_h) and electrons (μ_e). From the time-of-flight measurements of amorphous samples, the hole drift mobility was found to be on the order of 10^{-5} cm^2/volt sec at room temperature; however, no drift current was observed for electrons. A similar result regarding the electron drift mobility has been reported for both single crystal and

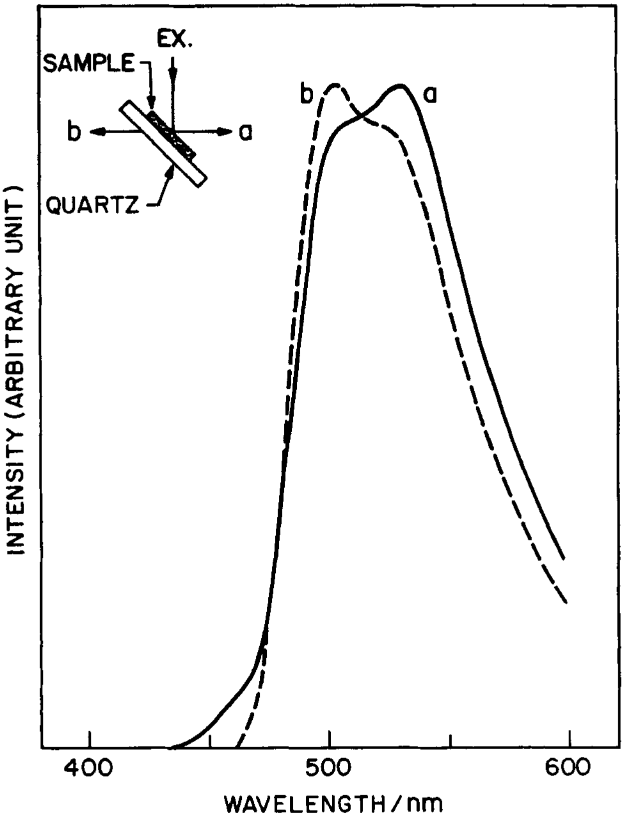

FIGURE 6 Corrected photoluminescence spectra as observed from the side facing surface of light beam incidence (curve a) and from the opposite side (curve b).

amorphous samples of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline.[19] One possible cause for the lack of drift current for electrons is the extremely small value of μ_e. In such a case, the recombination zone of both carriers would localize near the cathode side of the film in the steady state.

CONCLUSIONS

Significant levels of dc-voltage induced electroluminescence were observed in the sandwich-type EL cells of amorphous Py-1. The current was limited by the space charge; however, double injection of carriers occurred after the transition from the trapped SCL current process to a trap free SCL current-controlled process. The light emission was thought to arise from radiative decay of singlet excitons which were generated by recombination of holes and electrons and by annihilation of two triplet excitons. On the basis of photoluminescence data, it was concluded that the light emission zone was localized near the cathode side in the Py-1 film.

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