

# Short-term evolution of injection efficiency at metal/organic interfaces

*Andronique Ioannidis<sup>1,3</sup>, John S. Facci<sup>1,2</sup>, Martin A. Abkowitz<sup>1</sup>*

- 1. Center for Photoinduced Charge Transfer, University of Rochester, NY*
- 2. Xerox Corporation, Xerox Research & Technology, Webster NY 14580*
- 3. Xerox Corporation, Corporate Strategic Services, Webster NY 14580*

## Abstract

A contact forming phenomenon between a variety of metal contacts and organic charge transport layers has been previously reported whereby the hole injection efficiency of the contacts evolves from blocking to ohmic over time periods of up to 1 month. Two main processes, one slow and one rapid, were found to govern the injection evolution by using an experimental technique that combines field-dependent injection current measurements with time-of-flight drift mobility measurements on the same films. Results regarding the rapid process (1-3 hours) are now presented for a variety of organic interfaces, including a molecularly doped polymer of triarylamine (TPD) in polycarbonate, evaporated TPD films and films of the electroluminescent polymer MEH-PPV. The process occurs with evaporated metal contacts, with metal substrates and with liquid Hg, ie. independantly of the contact fabrication method. Variations of the intermolecular structure by organic surface treatment and by the use of sterically hindered TPD isomers suggest a reorganization at the organic surface on interface formation.

## Introduction

Fundamental questions concerning metal/organic interfaces are receiving much attention, stimulated by wide application of organic materials in electrophotography<sup>1</sup> and the rapidly expanding field of organic electronic devices. Contacts of metals to classical semiconductors and insulators are understood within the framework of band theory, where charge injection can be described as a function of interfacial energy barriers, as in the Richardson-Schottky theory of thermionic emission or Fowler-Nordheim tunnelling<sup>2</sup>. However, direct correlation to energy barriers is difficult to rationalize in most molecular materials where a distribution of energy states exists, carriers are localized and transport is by hopping. Notable models of injection and charge transport geared to hopping systems have been recently proposed, such as by E. Conwell and coworkers<sup>3</sup> and by H. Bässler and coworkers<sup>4</sup>. However, further development

has been limited by the dearth of experimental results amenable to theory.

An important limitation to the experimental study of metal/organic interfaces is the lack of direct measurements of the injection efficiency of contacts, since measured injection currents are also dependent on the charge transport properties of the material. In the present work, the properties of the interface are isolated from those of the bulk following a technique<sup>5</sup> that combines trap-free space charge limited currents with time-of-flight drift mobility measurements on a model system of a trap-free molecularly doped polymer. The findings are furthermore extended to other organic materials, both polymeric and oligomeric.

In previous work on metal-molecularly doped polymer(MDP) interfaces, this technique revealed an evolution in injection efficiency<sup>6,7</sup> when Au was sublimed onto the MDP of a TPD-doped polycarbonate. Measurements from the first minutes to several weeks after contact deposition show a contact that evolves from severely injection limited to ohmic over time. The initial blocking nature was contrary to expectations according to the relative workfunctions of Au and this MDP(ca.5.5eV) which are close enough to enable efficient injection of holes. The analysis of the kinetics<sup>7</sup> for the entire evolution suggested the operation of two processes, one which was slow and accounted for approximately one month of evolution, and a short-term process on a time scale of 3-5 hours, dependent on temperature. The possibility of Au penetration into the MDP was counterindicated in Transmission Electron Microscopy studies of the Au/MDP interface over time at a resolution of 10Å. The long-term process was identified with repair of the MDP surface from thermal damage when a single layer of metal is deposited at a given rate<sup>8</sup>. This process can be largely eliminated by performing a sequential, multilayered metal deposition, after which injection becomes ohmic within a few hours. The metal's crystallinity and morphology did not change over time.

Most significantly in the present context, it was also shown that the short-term process is not affected by the metal fabrication. This process is considered to arise from

the organic side of the interface and instigated by the presence of the metal. Accordingly, the present article investigates factors affecting this process and demonstrates a wider applicability to other types of organic material: a molecular glass of TPD and a polymer film of MEH-PPV.

## Experimental

The sample configurations used are shown in Fig.1a. MDP films were solution coated onto a carbon-filled polymer contact (MystR®) to thicknesses of 20-30  $\mu\text{m}$  from a 4 wt% methylene chloride solution of TPD and polycarbonate (40/60 wt% ratio). Films were slowly dried in a local atmosphere saturated with methylene chloride, cured for 30 minutes in a convection oven over a gradient of temperatures ending in 110°C, and finally allowed to cool to room temperature before evaporating the top metal contacts. All metal contacts were evaporated by resistive heating of the metal, producing contacts 220-250  $\text{\AA}$  thick.

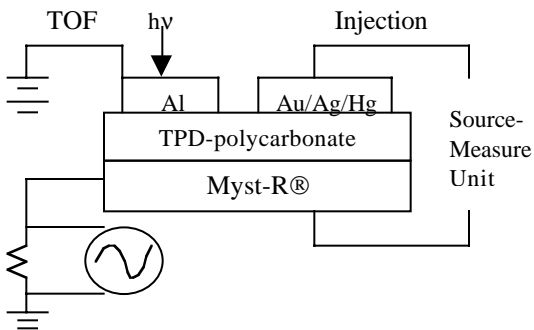


Fig.1a: Sample configuration and experimental arrangement

5-20  $\mu\text{m}$  thick films of 100% TPD were evaporated at a rate of 300A/s under a vacuum of  $1 \times 10^{-6}$  Torr. MEH-PPV was synthesized according to Hsieh et al.<sup>9</sup> and coated from a 1%wt. solution in Methylene Chloride; samples of 6-10  $\mu\text{m}$  were maintained and measured in a dry  $\text{N}_2$  atmosphere.

The small signal hole drift mobility,  $\mu$ , is obtained by measuring the time ( $t_{tr}$ ) required for a photoinduced charge packet to transit the sample thickness in a conventional time-of-flight (TOF) experiment<sup>10</sup>. The measurement of mobility enables the calculation of the trap-free space charge limited current, the maximum current that may be sustained by the bulk, of thickness  $d$ , according to Child's Law

$$J_{TFSLC} = 9/8 \epsilon \epsilon_0 \mu E^2 / d, \quad (1)$$

where  $\epsilon$  is the relative dielectric constant and  $\epsilon_0$  is the permittivity of vacuum. A measured current density that coincides with the calculated  $J_{TFSLC}$  classifies a material as trap-free. The ratio of the injected current density from an evaporated metal contact to  $J_{TFSLC}$  is defined as the contact injection efficiency (illustrated henceforth for Au),

$$\text{Injection Efficiency} = J_{Au} / J_{TFSLC} \quad (2)$$

Details of the rationale for this quantitative determination of injection efficiency have been previously discussed<sup>(5)</sup>. The hole drift mobility, monitored at the Al contact between successive  $J_{Au}$  measurements in the same film, remains invariant with time, ensuring that any changes in  $J_{Au}$  are not due to a change in bulk transport properties. The injection current from the bottom MystR® contact, which is ohmic for hole injection, is also monitored and serves as another control measurement.

Contact ohmicity of MystR® is shown in Fig. 1b, where the calculated TFSLC densities,  $J_{TFSLC}$ , coincide with the measured dark injection current from MystR®,  $J_m$ .

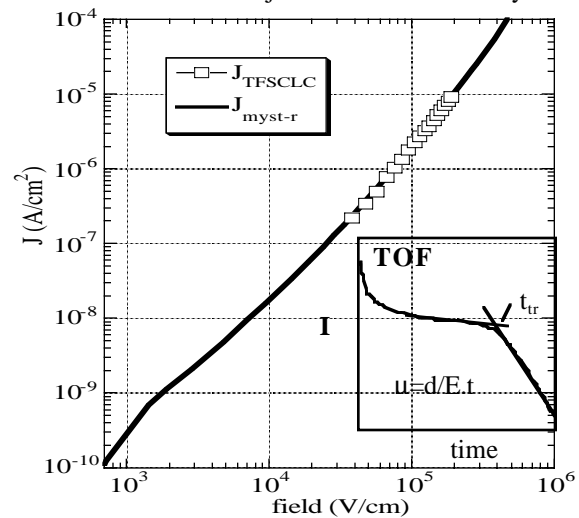


Fig.1b: Ohmic injection from Myst-R®

An equivalent measure of injection efficiency for a contact on the present transport system is therefore

$$\text{Injection Efficiency} = J_{Au} / J_m = J_{Au} / J_{TFSLC} \quad (3)$$

Injection efficiency was computed at a common field,  $1 \times 10^5$  V/cm for all comparisons.

## Results

Fig.2 shows typical current vs. voltage parametric in time for a Au/MDP/MystR® device, where the top Au contact was deposited sequentially. The current appears severely injection limited immediately following contact (10 minutes after contact deposition) and increases with time. The injection becomes ohmic within 12 hours, which is shown by its close coincidence to the injection current from the bottom contact, MystR®, also indicated in Fig.2. This is representative of contacts that are evaporated sequentially. However, while the conditions of evaporation of the metal virtually eliminate long-term evolution, variation in metal fabrication produced no effect on either the initial blocking behavior or on the short-term process seen in figure 2.

Fig.3 shows results of a manipulation of the organic material's surface that does affect both the initial blocking

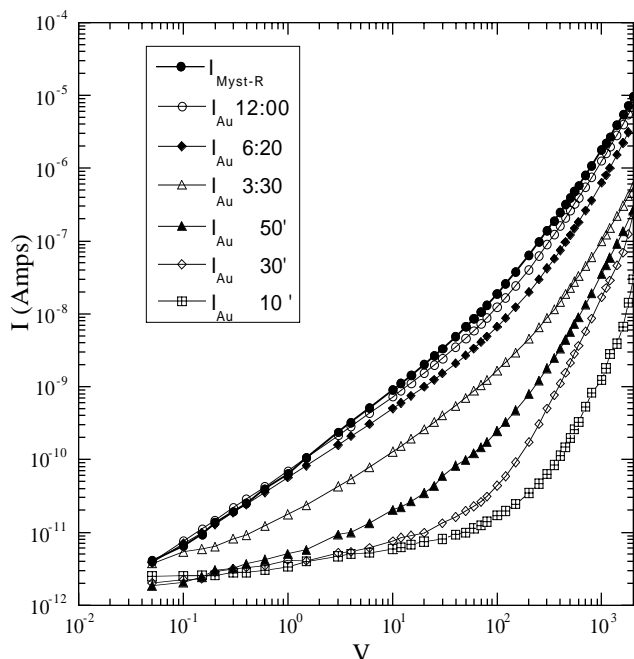


Fig.2 Dark current versus voltage parametric in time for a sequentially deposited Au contact on a  $20\mu$  film of 40/60wt% TPD/polycarbonate; shows short-term injection evolution.

nature and the early injection behavior. After casting and plasticizing the MDP, it was exposed to the vapors of its solvent, methylene chloride. Up to 30 minutes exposure produced no change in either the TOF mobility or the injection from the lower contact, suggesting that the bulk material has not become significantly wetted.

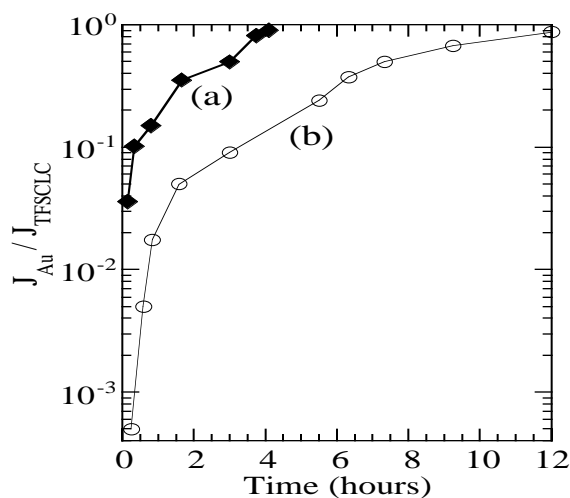


Fig.3 a) Injection efficiency for vapor-doped 40/60 wt% TPD/polycarbonate with sequentially evaporated Au contact, compared to b) equivalent sample not exposed to solvent.

However, Fig.3a shows that injection efficiency of a Au contact deposited after vapor doping is ca. 2 orders of magnitude higher than without vapor doping, as can be seen

by comparing to Fig.3b where the injection efficiency for the untreated film of Fig.2 is also shown. Similarly, the injection efficiency in Fig.3a evolves to ohmic within 4 hours. Vapor doping after Au deposition has the same effect.

These results would suggest that either/both the swelling of the MDP surface accelerates the early process, or there is solvent chemistry at the Au-organic interface, especially as methylene chloride can release  $\text{Cl}^-$ . A possible metal-MDP chemical reaction was however not detected by XPS studies performed over a month using both Au and Ag top contacts. Also, the use of other solvents, chlorobenzene and THF, produced a similar effect. Solvent chemistry at the metal-organic interface is thus not supported by the results.

Finally, the results below in Fig.4 experimentally preclude the possibility of any residual thermal damage effect to the organic surface by sequential metal evaporation, since injection evolution is also observed for Ag substrates, ie. where the organic film is coated onto preformed metal films.

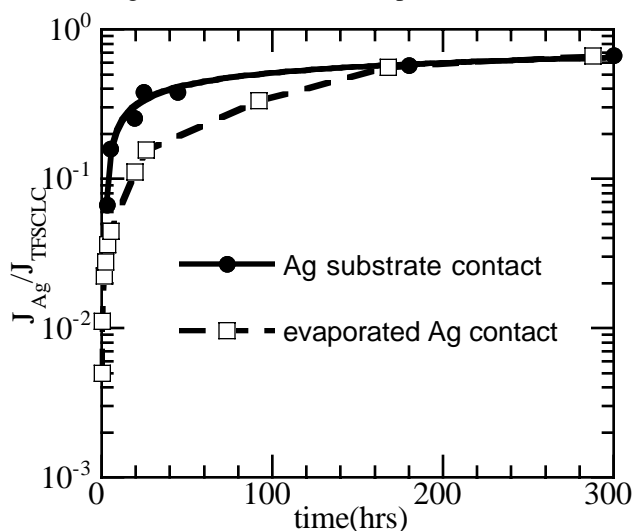


Fig.4 Injection efficiency as a function of time for Ag substrate and sequentially evaporated Ag top contact on a film of 40/60 wt% TPD/polycarbonate - isolating the "short-term" process.

In the case of Ag, the evolution process is much slower than for Au and injection maximizes, at a non-ohmic level, only after 300 hours. These results then indicate that the nature of the metal affects the rate of the process. The slower evolution enabled capturing the effect when using a metal substrate, as the process is still in operation at the time of first measurement after substrate contact (3 hrs, cf. 10 minutes when measuring after evaporated top contacts). The process has also been observed with a Hg (liquid) contact<sup>8</sup>.

Consideration of the above results in conjunction with earlier work<sup>6-8</sup> eliminates a wide variety of mechanisms and raises the possibility that the injection evolution appearing immediately following contact to the metal arises from a molecular reorganization at the organic surface. If such were the case, then intermolecular interactions should affect the

process. Swelling the surface by vapor doping may be expected to decrease molecular interaction and the results of Fig.3 then indicate that this decrease has the effect of accelerating the process. Indeed, the converse effect is observable by increasing the concentration of the molecular dopant, TPD, thus increasing the molecular interactions.

The extreme case is shown in Fig. 5, where the process is dramatically slower for evaporated Au on a sublimed film of 100% TPD. At the same time, the use of a sublimed film precludes now any possibility of a solvent effect.

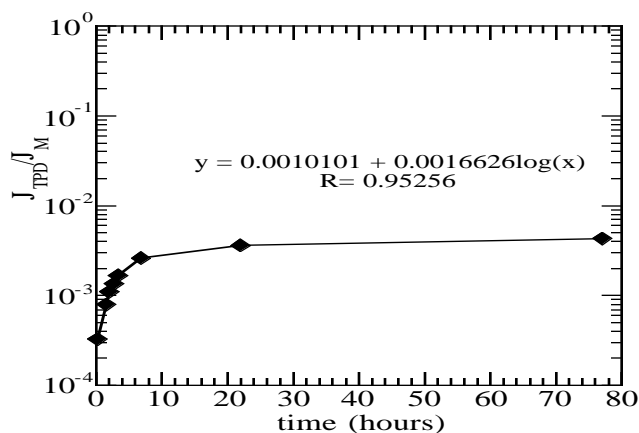


Fig.5 Injection efficiency evolution for sequentially evaporated Au on a  $10\mu$  glassy film of evaporated 100% TPD.

In addition, preliminary measurements using sterically hindered TPD, where methyl substituents on the central rings hinder rotation, do not show injection evolution. Thus molecular rotational freedom is implicated in the process.

Finally, the same process is found to operate at a metal-polymer interface, illustrated in Fig.6 for a  $6\mu$  sample of Au/MEH-PPV/Myst-R. This then removes the possibility of a TPD-specific process and expands the scope to include not only a molecularly doped polymer and a small molecule glass but also an (undoped) electroluminescent polymer.

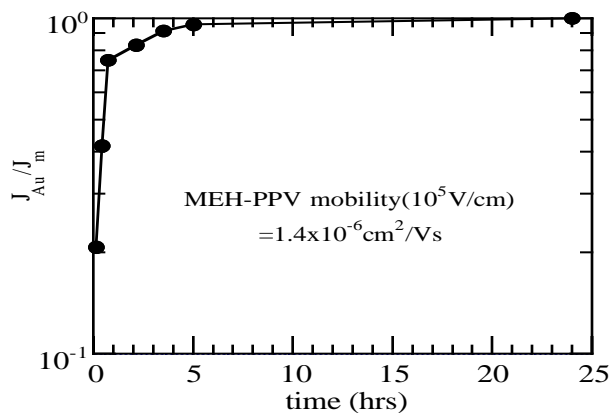


Fig6.Short-term evolution in injection efficiency for a device of Au/MEH-PPV( $6\mu$ )/Myst-R

## Conclusion

Experimental manipulations geared to isolating and characterizing the short-term component of a previously identified injection evolution phenomenon have now been presented. The short-term evolution is shown to be independent of contact manufacturing and not specific to one metal, though the rate of evolution is affected by the choice of metal. The functional form of the process, illustrated in Fig.5, is the same across different metals, differing in time-constant and prefactor. The rate of the process, and indeed whether or not ohmic injection is achieved, is strongly dependant on the state of the organic surface during contact formation. Surface treatment and concentration variations geared at varying intermolecular interaction strength suggested that there is a reorganization at the organic surface when it is placed in contact with the metal. This reorganization is facilitated by weaker interactions (greater volume fraction per molecule) and inhibited when the surface molecular interaction strength is increased in the same material. Finally, the process is shown to operate in three different types of organic film – a solution-coated MDP, an evaporated molecular glass and a solution-coated electroluminescent polymer. The characterization of this process suggests surface treatment options for improving injection efficiency and a previously unsuspected mechanism that may factor into aging phenomena in organic devices.

## References

1. P.M. Borsenberger, D.S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, NY (1993).
2. M. A. Lampert and P. Mark, *Current Injection in Solids*, Academic Press, New York (1970).
3. E.M.Conwell, *Handbook of Organic Conductive Molecules and Polymers*, Vol.4, pg.1, John Wiley & Sons (1997)
4. H. Bässler, *Phys. Stat. Sol.* **175**, 15 (1993).
5. M. A. Abkowitz, D. M. Pai, *Phil. Mag. B* **53**, 193 (1986)
6. M. A. Abkowitz, J. S. Facci,, J. Rehm, *J.Appl.Phys.* **83**, 2670 (1998)
7. A. Ioannidis, J. S. Facci, M. A. Abkowitz, *J. Appl. Phys.* **84**, 1439 (1998).
8. A. Ioannidis, J. S. Facci , M.A. Abkowitz, *J.Imag.Science and Technology*, **43**, 242 (1999).
9. B. R. Hsieh, Y. Yu, A. C. VanLaeken, H. Lee, *Macromolecules* **30**, 8094 (1997)
10. A. R. Melnyk and D. M. Pai, *Determination of Electronic Optical Properties*, Vol. 8, John Wiley & Sons, NY (1993).

## Biography

Andronique Ioannidis received a Masters in Solid State Physics from Concordia University in 1993 and a Ph.D. in Material Science from the National Research Institutes of the University of Quebec in 1997. Since 1998 she has been a project manager in Photoreceptor Technology at the Corporate Strategic Services Organization of Xerox Corp. in Webster, NY. Research interests focus on charge generation, transport and injection in organic materials. She is a member of the IS&T and the Materials Research Society.