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Effect of Metal Contact Fabrication on the Charge Injection Efficiency of Evaporated Metal Contacts on a Molecularly Doped Polymer

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We previously reported that contact injection efficiencies are amenable to direct measurement in thin trap-free hole transport polymer films by a technique combining time-of-flight bulk mobility measurements with steady state current densities measured at the contact under test. In the present article, films of a trap-free molecularly doped polymer, TPD/polycarbonate, are solution coated onto a carbon-filled polymer substrate that is demonstrably ohmic for hole injection. Thermally evaporated Au and Ag as well as liquid Hg form the top contacts. Field dependent contact injection efficiencies are computed from the combined measurements and monitored over time. A persistent pattern in the evolution of contact injection efficiency with time is revealed. Invariably contact injection efficiencies evolve by orders of magnitude from initially blocking to ohmic or to an equilibrium value dependent on the nature of the metal. For thermally evaporated Au contacts, coating studies suggest that the slow stage in the observed two-stage evolution of contact formation represents a process of recovery from damage to the transport layer's surface caused by the accumulating hot Au atoms. Such a process is not observed for substrate Au. Comparisons of the evolution in injection efficiencies of evaporated Ag contacts with substrate Ag, as well as of liquid Hg contacts, demonstrate that the initially blocking nature of the contact and a fast evolution process are not associated with recovery of the interface from thermal damage but are probably a more general aspect of contact formation.

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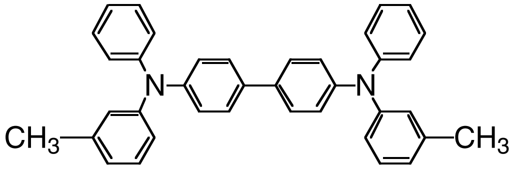
Introduction

Fundamental questions concerning metal/organic interfaces are receiving much attention, stimulated by the wide application of organic films in electrophotography[1] and in the rapidly expanding field of organic electronic devices.[2] In these applications, the manner in which electrical contact is made to the molecular material is ultimately critical to device operation. Contacts of metals to conventional semiconductors and insulators are interpreted[3] within the framework of band theory. However, it is difficult to rationalize the application of models developed for band-type materials to the case of disordered molecular materials (e.g., polymers and small molecules) where carriers are localized and transport involves discrete hopping within a distribution of energy states. An issue of current interest is the form of the correlation of charge injection into disordered organic materials with the interfacial energy barrier as estimated from the relative workfunctions of the interface materials. However, "workfunctions" of molecular materials are either inferred from electrochemically determined oxidation potentials or measured microscopically in ultra-high vacuum.[4] These may not relate directly to barriers formed under less pristine conditions for example those typically encountered using solution coating methods. Furthermore, it is unclear how band-type treatments of energy barriers, such as those incorporating the Richardson-Schottky theory of thermionic emission or the Fowler-Nordheim tunneling model,[5] can be simply recast to apply to disordered molecular materials. Models of injection and charge transport geared specifically to hopping systems have in fact been recently proposed by Conwell and coworkers[6,7] and by Bässler and coworkers.[8–11]

The problem of separating charge transport and interface effects on the injection current is clearly solved in the case of trap-free molecularly doped materials. The present study is based on a method previously described[12,13] for obtaining the injection efficiency of a contact on a trap-free unipolar transport medium, e.g., a molecularly doped polymer (MDP). The contact injection efficiency of an evaporated-Au/MDP interface is probed directly by comparing the small signal time-of-flight (TOF) behavior with field dependent steady state current measurements. The trap-free MDP is a glassy solid solution of an electroactive triarylamine derivative TPD, (shown below) in an inert polycarbonate matrix. By inert it is meant that charge transport does not occur through states associated with the polymer, even though the mobility can vary by orders of magnitude depending on the nature of the polymer.[14]



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The metal contact is deposited by thermal evaporation, which has been the method of choice for metal contact formation in organic devices such as Light Emitting Diodes (LEDs) or Thin Film Transistors (TFTs).[15] In the following we analyze the evolution of hole injection efficiency from an evaporated Au contact on the MDP as it increases over time from emission limited or blocking to the maximum efficiency which in the case of Au is an ohmic contact. This time dependent process is not observed when the MDP is coated onto a preformed Au substrate which is initially ohmic. We describe injection evolution for the evaporated Au contact in detail for a series of samples, characterizing the time and temperature dependence of the phenomenon to elucidate the nature of contact efficiency recovery process. It proves fruitful to extend these measurements to Ag and liquid Hg contacts.

Previous analysis[16] of the kinetics of the evaporated-Au/MDP interface formation revealed a non-linear behavior, composed of a rapid increase in injection efficiency at early times (hours) followed by a much slower increase over a period of weeks. The results were represented by two exponentials with associated time constants, and thus two main processes were distinguished. The rate of the evolution at early times was temperature dependent and an Arrhenius plot yielded an activation energy of ca. 0.3 eV. In order to investigate what mechanisms may be responsible for these two evolution processes, it is helpful to regard a sample as a three-component system, comprised of the MDP, the Au and their interface. A major mechanism postulated to operate with metal contacts on organic thin films is the diffusion of metal atoms arriving from the vapor phase into the transport film as recently reported.[17] For example, metal diffusion is observed in perylenetetracarboxylic dianhydride (PTCDA) thin films coated with reactive metal contacts (Al, Ti, In, Sn) but is not observed in the case of the least reactive metals Au and Ag. For the MDP the possibility of Au penetration and diffusion was investigated[16] by transmission electron microscopy (TEM). Results of these studies showed the interface to be abrupt to within 1 nm and invariant over time, i.e., no Au/MDP interpenetration was observed over a period of at least one month.

The present work describes the effect of Au contact fabrication on hole injection efficiency. Two distinct time dependent processes governing the evolution of the contact injection efficiency immediately after fabrication are identified. To test the generality of this result, comparisons with other metal contacts, e.g., Ag and Hg, have also been carried out. The slow or long-term process is correlated with metal evaporation conditions. The underlying mechanism is discussed. On the other hand the rapid or short term process is shown to be less sensitive toward the detailed conditions of metal fabrication and appears to be a persistent feature of the MDP/metal interface formation. Manipulations geared toward investigating the role played by the organic surface in the evolution of hole injection efficiency and the generality of the observations for other organic materials will be reported elsewhere.

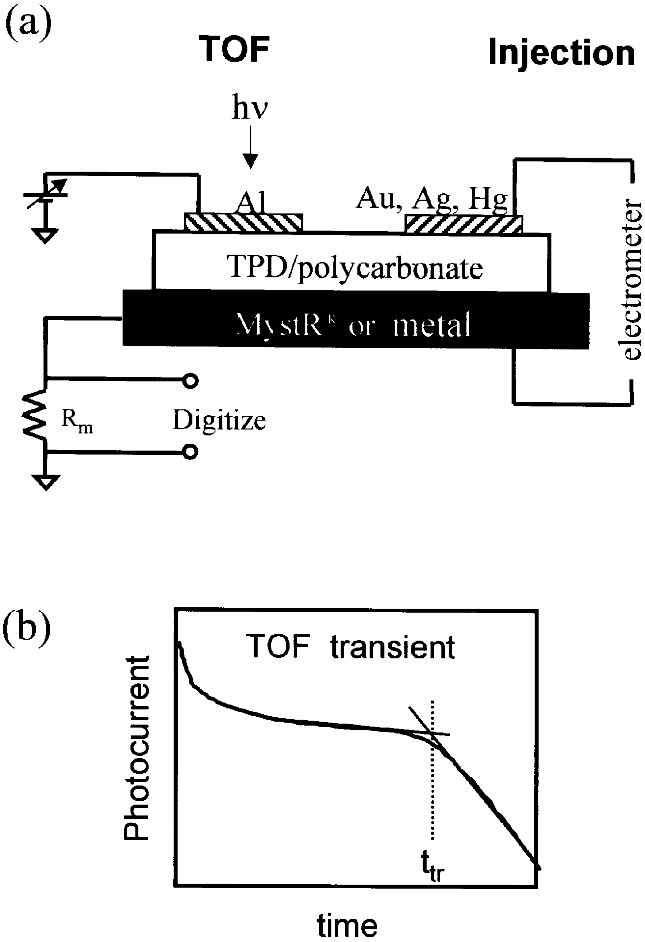

Figure 1. (a) Schematic diagram of the experimental sample configuration. 40 wt% films of TPD/polycarbonate are coated onto a MystR® substrate which is ohmic for injection into the TPD layer. The Al top contact is used for obtaining TOF results and the test contacts are vapor deposited Au or Ag as well as liquid Hg fitted onto the same film as the Al contact. (b) Graphical method for obtaining the transit time of carriers from the knee of the small signal TOF photodischarge curve.

Experimental

The sample configurations used are shown in Fig. 1(a) and an illustration of the graphical method used to determine hole transit time and hole drift mobility from the knee of the TOF transient photodischarge curve is presented in Fig. 1(b). Molecularly doped polymer films were solution coated onto a carbon-filled polymer contact (MystR®) to thicknesses of 20–30 μm from a 4 wt% methylene chloride solution of TPD and polycarbonate (40/60 wt%). Films were slowly dried in a local atmosphere saturated with methylene chloride, cured for 30 min 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 source, producing films of 220–250 Å in thickness.

The small signal hole drift mobility, μ, 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, such that[18]

$$\mu = d / E\, t_{tr} \qquad (1)$$

where d is the sample thickness and $E = V/d$ is the average electric field. The TOF experimental arrangement has been described previously.[12,13,19]

The measurement of μ enables the calculation of the trap-free space charge limited current, the maximum current that may be sustained by the bulk, according to Child's Law,[5]

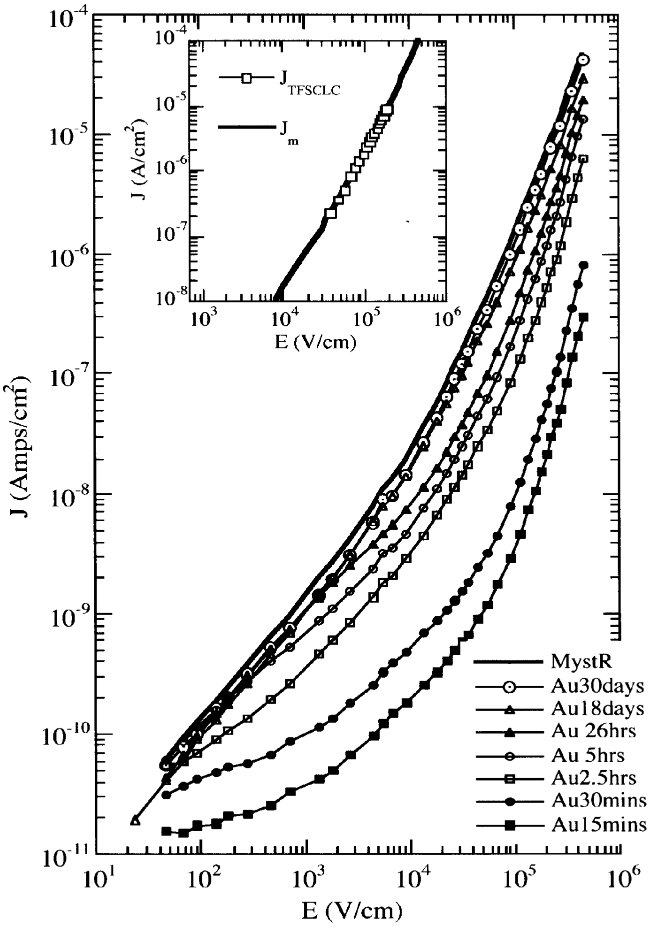

Figure 2. Temporal evolution of the hole injection current from a 220 Å Au contact evaporated at 10 Å/sec onto a thin film of 40 wt% TPD/polycarbonate. The latter are compared with J_m which represents the level of ohmic injection current. Note that the top Au contact evolves from emission limited to ohmic over the course of the analysis (15 min to 30 days). Inset: comparison of J_{TFSCLC} (open squares), the trap-free space-charge limited current density calculated from hole drift mobility in 40 wt% TPD/polycarbonate with J_m, the steady state dark injection current from the MystR® substrate. The coincidence of the two current densities demonstrates that the substrate is ohmic for injection into 40 wt% TPD/polycarbonate.

$$J_{TFSCLC} = (9/8)\,(\varepsilon\,\varepsilon_o\,\mu\,E^2/\,d), \qquad (2)$$

where ε is the relative dielectric constant and ε_o is the permittivity of vacuum. A measured current density that coincides with the calculated J_{TFSCLC} is the necessary and sufficient condition to classify a material as trap-free. However, in the case of TPD/polycarbonate, there is also well known experimental confirmation as xerographic charging/discharging measurements consistently reveal no hole trapping at either short or very long time scales. The ratio of the injected current density from an evaporated metal contact against J_{TFSCLC} is defined to be the contact injection efficiency (illustrated henceforth for Au), i.e.,

$$\text{Injection Efficiency} = J_{Au}/\,J_{TFSCLC}. \qquad (3)$$

Details of the rationale for this quantitative determination of injection efficiency have been previously discussed.[12,13,19] 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 the bulk transport property of the film. The injection current from the bottom MystR® contact which is ohmic for hole injection is also monitored periodically and serves as another control measurement. The contact ohmicity of MystR® is illustrated in the inset of Fig. 2, which demonstrates that the calculated trap-free space-charge limited current densities J_{TFSCLC} (open squares) coincide with the measured steady state dark injection current (solid line) from the MystR® substrate J_m. An equivalent measure of injection efficiency for a contact under test in the present transport system can therefore be obtained by direct comparison of the injection current at the test contact to that at the MystR® contact J_m, viz.,

$$\text{Injection Efficiency} = J_{Au}/\,J_m = J_{Au}/\,J_{TFSCLC}. \qquad (4)$$

Injection efficiency is computed at a common field, 1×10^5 V/cm.

Scanning electron microscopy (SEM) and x-ray diffraction (XRD) measurements on 220 Å thick Au films deposited at 10 Å/s were obtained as a function of time following deposition, allowing the contact to age under ambient conditions. The latter analyses were done in parallel with injection efficiency measurements.

Results and Discussion

Hole injection currents from evaporated Au and Ag contacts, as well as liquid Hg, were obtained as a function of field and time under ambient conditions. Current density versus field data for all metal/MDP samples show no hysteresis and results were reproducible for several sample sets. In the case of Au, measurements were performed under a variety of metal evaporation conditions. Typical J_{Au} versus field data parametric in time are shown in Fig. 2 for a film of 40 wt% TPD/polycarbonate on MystR® at 23°C. The figure shows the evolution in J_{Au}, compared to the time invariant J_m curve.

SEM and XRD measurements were performed in order to investigate the possibility that the morphology or surface texture of the metal film itself is changing with time, potentially affecting the contact workfunction or actual contact area. The XRD results show two peaks of equal amplitude corresponding to Au(111) and Au(222) and both their amplitude their relative ratios remain invariant from 1 h to 2 weeks after Au deposition. Note that this corresponds to a time span encompassing both evolution processes. Scanning electron microscopy results were obtained over the same time span at 300 nm, 600 nm and 1 µm resolutions and show a cracked Au film morphology. SEM results reveal a porous film in which the density and size of cracks does not, however, change in time. Therefore, the evolution in injection efficiency cannot be readily assigned to changes in metal film structure.

A further possibility related to metal fabrication is that during the metal evaporation, the energetic Au atoms or the accumulation of a hot Au layer on the MDP may in some way damage the MDP surface. Such damage may be repaired over time by polymer chain or small molecule diffusion which could act to replace damaged surface molecules and indeed the time scale of the slow evolution is not inconsistent with such a mechanism.[20] Accordingly, a systematic variation of metal evaporation conditions was performed. A comparison of four evaporation conditions is shown in Figs. 3(a)–3(d). The

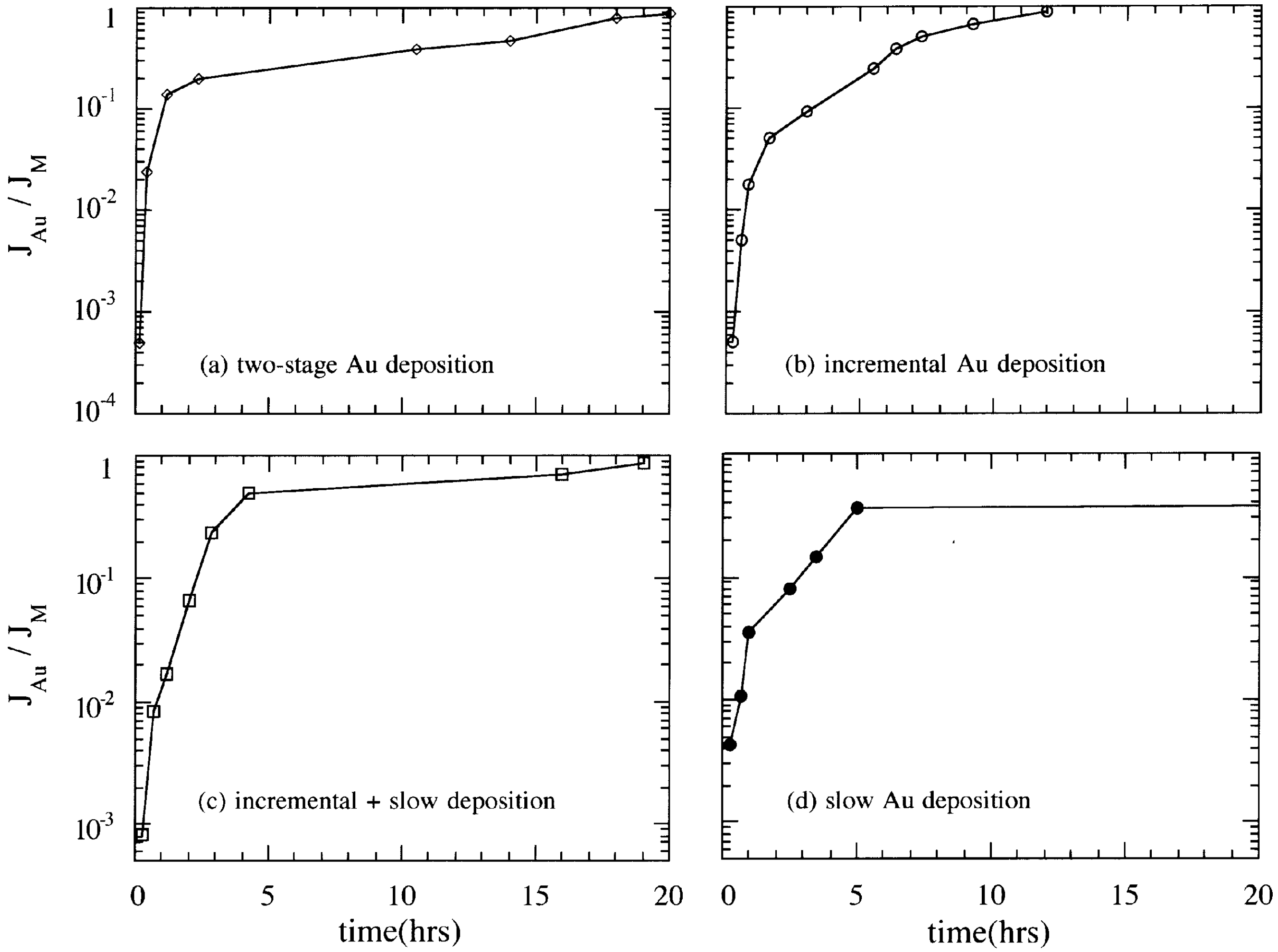

Figure 3. Temporal evolution of the injection efficiency at 1.0 × 10^5 V/cm of evaporated Au contacts on 40 wt% TPD/polycarbonate as a function of Au deposition conditions. All Au contacts are 220 Å. Panel A: Au is deposited in two steps, 50 Å and 170 Å, at 10 Å/sec. Panel B: 11 layers of 20 Å each at 10 Å/sec. Panel C: 11 layers at 2 Å/sec. Panel D: a single continuous step at 2 Å/sec. In all cases the injection efficiency is initially blocking.

Au contacts shown in Figs. 3(a)–3(c) are fabricated by an incremental or sequenced deposition process. The deposition of each layer is separated by 1–2 min during which the source is not heated and a shutter covers the MDP surface. Specifically the Au contact in Fig. 3(a) is deposited in two stages, a 50 Å and a 170 Å layer at 10 Å/s; the Au contact of Fig. 3(b) is composed of 11 20 Å depositions at 10 Å/sec and finally the Au contact of Fig 3(c) is composed of 11 20 Å depositions at 2 Å/s. Note that all layered depositions result in a dramatic reduction in the time scale of the long-term evolution process. Each of the evaporated Au contacts deposited under these conditions achieves contact ohmicity in under 20 h. This is significantly shorter than the ~800 h required to achieve contact ohmicity for a continuous Au deposition at 10 Å/s as depicted in Fig. 2. Decreasing the rate of Au deposition from 10 Å/s to the 2 Å/s in a continuous deposition of the Au contact does not significantly reduce the time required to achieve contact ohmicity from 800 h as suggested by Fig. 3(d), i.e., no change is noted in the long term process. These manipulations of metal evaporation conditions therefore suggest that damage inflicted of the MDP surface is thermally induced by the arrival of hot Au atoms during a typical continuous evaporation and this damage can be virtually eliminated if Au is deposited in multiple layers separated by short cool-down periods.

Especially notable in Fig. 3 is that in no case is the initial blocking nature of the interface affected nor the rapid initial rise in injection efficiency. Therefore, in agreement with the prior kinetic studies,[16] these results indicate strongly that there are indeed two distinct processes governing the evolution in contact behavior. However, in order to more fully understand the nature of this behavior, the behavior of contacts which are fabricated under conditions that ensure the interface suffers minimal thermal damage was investigated. Toward this end the injection behavior using pre-formed metal substrates was investigated. In this case the metal is evaporated onto glass and the MDP film is then solution coated onto the metal in the usual manner.

Injection efficiency results for Au substrate contacts showed these contacts were always ohmic at the minimum measurement time of ca. 3 h. The minimum measurement time is established by the sample preparation steps of solution casting, evaporation, curing and evaporation of the top contact.

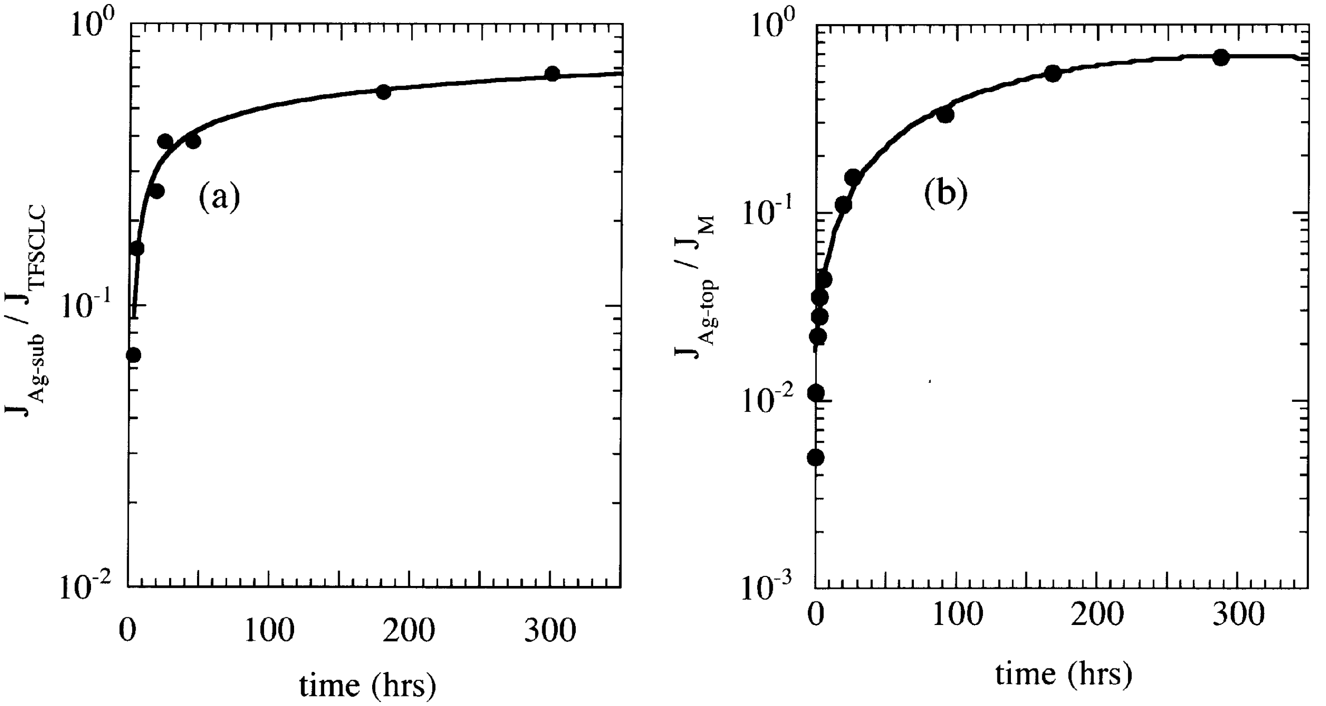

Figure 4. Comparison of the temporal evolution of the injection efficiency J_{Ag}/J_{TFSCLC} for a freshly deposited Ag substrate (a) with the injection efficiency J_{Ag}/J_m of an evaporated Ag top contact (b).

In contrast with the above results, Fig. 4(a) presents injection efficiency versus time for a sample of Al/MDP/Ag-substrate. In the latter case injection efficiency is computed from the TFSCLC obtained from TOF mobility measurements. The injection efficiency for the Ag-substrate sample is monitored beginning 3 h after Ag substrate is contacted with the polymer casting solution. As distinct from the case of Au substrate contact, an evolution in injection efficiency is observed strongly suggesting a contact forming process independent of the effects of interfacial damage arising from metal deposition.

Figure 4(b) shows the injection efficiency (J_{Ag}/J_m) versus time for a comparable MDP film with an evaporated Ag top contact that was deposited layer-by-layer. It is anticipated from the results depicted in Figs. 3(a)–3(c), that thermally induced interfacial damage from Ag contacts fabricated under these conditions is minimized. Comparison of Figs. 4(a) and 4(b) indicate that the evolution of injection efficiency in both the Ag substrate and evaporated Ag contact are comparable. This comparison of injection from a Ag substrate to that from a Ag layered top contact suggests that the layer-by-layer deposition eliminates most, but not all of the effect of metal deposition. Note that steady state injection efficiency of 0.6 is also similar in both cases. Ag contacts, unlike Au, never become ohmic for injection of holes into the MDP. This is consistent with the workfunction of Ag which is ca. 0.5 eV less than that of Au.[21] A further comparison in time scales between Fig. 4(b) and layered Au contacts in Figs. 3(a)–3(c) indicates that the "fast" process is markedly slower for the evaporated Ag (top) contact. On this basis Ag was chosen as the substrate metal in order to maximize the chance of observing any relaxation behavior because measurements cannot be performed until after the MDP film has been cured.

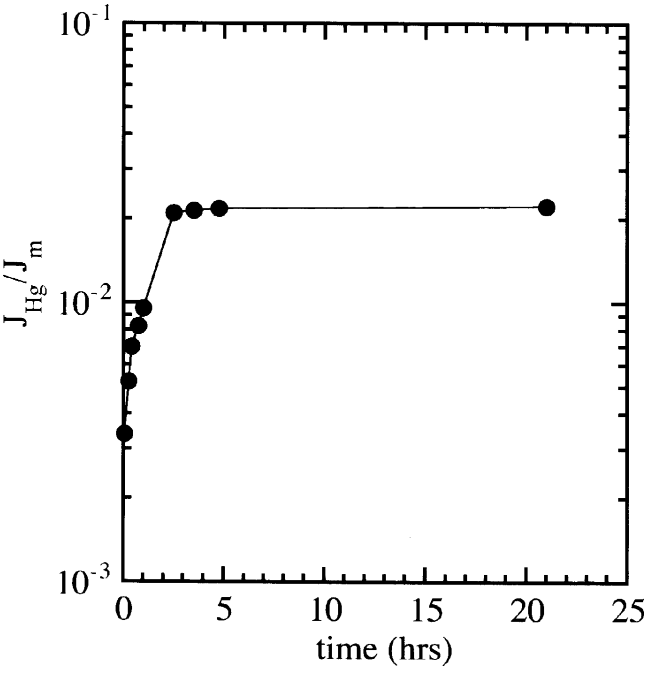

Figure 5. Temporal evolution of the injection efficiency J_{Hg}/J_m for a liquid Hg droplet contact made to a 40 wt% TPD/polycarbonate film. The area of the liquid contact is defined by a Teflon template containing a 0.316 cm^2 hole.

Finally, Fig. 5 depicts injection efficiency versus time for a Hg/MDP/MystR® sample, showing that contacts of a liquid Hg droplet of well defined area made to the sample surface also give rise to an evolution in injection behavior. This contact is particularly interesting in that any possibility of thermal damage to the interface is precluded. In addition, it is also possible to begin measurements of current density almost immediately after top contact formation. Taken together, these results indicate time dependent contact formation processes operate with a variety of metals under a variety of fabrication conditions. In particular a persistent “fast” contact formation process is operational, independent of the nature of the top contact and the manner in which it is fabricated.

Conclusion

The time dependence of the injection efficiency from evaporated Au into a trap-free molecularly doped polymer has been observed for various metals under different fabrication conditions. Differently prepared Au, Ag and Hg contacts all show an initially emission limited hole injection efficiency into the MDP and this efficiency increases over time. Two processes governing the evolution in efficiency can be distinguished for *evaporated* Au and Ag contacts, consistent with earlier analyses of the kinetics of injection evolution from evaporated Au. In the case of Au, whose workfunction is near that of the MDP (~5.5 eV) the injection current becomes ohmic for both substrates and evaporated top contacts. No change in metal morphology or surface texture over time was detected. A systematic variation of the conditions of metal evaporation shows that a slow, long-term component of the evolution is due to the method of evaporation and can be virtually eliminated by performing a layer-by-layer metal deposition. This particular solution to the fabrication problem indicates that the MDP surface is thermally damaged during a typically rapid metal deposition of energetic Au accumulated continually on the sample surface. The long-term evolution process would then reflect recovery of the MDP surface. This recovery may be due to polymer chain motions that act to replace damaged segments at the surface or diffusion of the molecular dopant, TPD, that would restore a surface concentration of TPD depleted by sublimation during the heating of the MDP surface. On the other hand we have distinguished an early time or rapid component of the evolution in injection efficiency which is determined to be largely independent of a degradative process of kinetic origin. ▲

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