



Enhanced bulk conductivity and bipolar transport in mixtures of MoO_x and organic hole transport materials

Baolin Tian, Dayan Ban, Hany Aziz*

Department of Electrical and Computer Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

ARTICLE INFO

Article history:

Received 12 July 2012

Received in revised form 18 March 2013

Accepted 21 March 2013

Available online 2 April 2013

Keywords:

Molybdenum oxide (MoO_x)

Lateral structure

Bulk conductivity

Bipolar transport

ABSTRACT

We study the conductivity of thin films of molybdenum oxide (MoO_x) mixed with an organic hole transport material, such as N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine or 4',4''-tri(N-carbazolyl)triphenylamine, in lateral test devices. Contrary to previous reports, the conductivity of the mixture is found to exceed that of neat MoO_x, exhibiting ~5 orders of magnitude higher conductivity in comparison to the neat films. Studies also show that the mixing enhances both hole and electron transport. The higher conductivity may be attributed to a higher concentration of "free" carriers in the mixture, as a result of the formation of a charge transfer complex between the MoO_x and the hole transport material. The findings shed light on the potential of hybrid composites of inorganic and organic materials in realizing enhanced conductivity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Due to its benefits on device performance, the use of molybdenum oxide (MoO_x) as a hole injection and/or transport material in organic light emitting devices (OLEDs) and organic solar cells (OSCs) has gained momentum rapidly in recent years. In case of OLEDs, its use as a hole injection layer [1–5] or as a dopant [6–10] in the hole transport layer, can lower driving voltage and improve stability [11–13]. In OSCs, its use as an anode buffer layer proved beneficial to power conversion efficiency [14,15]. Its high optical transmittance, low evaporation temperature, and the fact that it can be doped into organic semiconductor materials at high concentrations (~50%) without negatively impacting charge transport [13,16] have spurred the interest in studying it in mixtures with charge transport materials [13,17]. Shin et al. [13] showed that doping N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) with MoO_x resulted in higher conductivity in comparison to neat NPB, and attributed the effect to charge transfer between MoO_x and NPB. Using C–V measurements, they showed that the carrier density in MoO_x:NPB mixtures was several orders of magnitude higher than that in neat NPB. Ma et al. [17] also showed that the conductivity of NPB increased rapidly on doping with MoO_x. However the trend saturated at higher MoO_x concentrations, causing the conductivity of the mixture to approach that of neat MoO_x. A similar trend was observed by Matsushima et al. [10] on doping alpha-sexithiophene with MoO_x, again showing that the conductivity of the doped film was higher than that of neat alpha-sexithiophene, but lower than that of neat MoO_x film.

In this work, we study the conductivity of thin films of molybdenum oxide (MoO_x) mixed with a hole transport material (HTM), such as N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) or 4',4''-tri(N-carbazolyl)triphenylamine (TCTA) in lateral test devices in addition to the more conventional vertical test devices. The lateral test devices are used in order to better resolve and differentiate between contribution from injection and bulk transport. Contrary to previous reports, the conductivity of the mixture is found to exceed that of neat MoO_x, exhibiting ~5 orders of magnitude higher conductivity in comparison to the neat films. Studies also show that the mixing enhances both hole and electron transport. The findings shed light on the potential of hybrid composites of inorganic and organic materials in realizing enhanced conductivity.

1.1. Experimental details

For comparing conductivity of thin films of MoO_x, HTM and MoO_x:HTM ($y: (100-y)$), (where y represents the % volume concentration of MoO_x in the mixture), test devices of two different structures, fabricated on glass substrates, are employed: (1) a standard vertical structure in which a ~100 nm thick layer of the material to be tested is sandwiched between indium tin oxide (ITO) and Ag (or Mg:Ag) electrodes, and (2) an unconventional lateral structure in which a ~100 nm thick layer of the material is coated onto two Ag electrodes (~25 nm thick), both pre-coated on the same substrate, and separated by a ~26 μm gap. NPB and TCTA are used as HTMs. All layers and the metal electrodes are fabricated by thermal deposition at a rate of 0.5–3 Å/s in vacuum at a base pressure $< 5 \times 10^{-6}$ Torr ($\sim 6.67 \times 10^{-4}$ Pa) on pre-cleaned (using acetone and isopropyl alcohol baths, followed by UV ozone treatment) substrates. The MoO_x:

* Corresponding author.

E-mail address: hany.aziz@ecemail.uwaterloo.ca (H. Aziz).

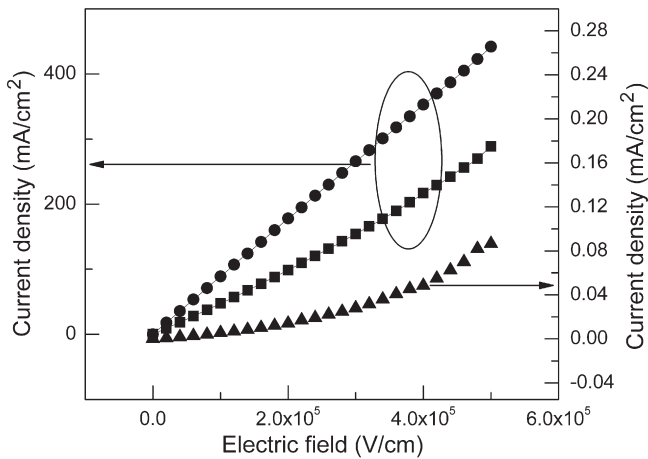


Fig. 1. Current density versus electric field of 100 nm of MoO_x, NPB and MoO_x:NPB (50:50) in a standard vertical structure.

HTM mixtures were formed by co-evaporation of the MoO_x and HTM from individually controlled sources in the desired ratio. The deposition rate of each material was controlled using quartz crystal oscillators. The substrate was kept at room temperature during the deposition. The current–voltage (I–V) measurements were carried out using an Agilent 4155C semiconductor parameter analyzer. All tests were carried out in a nitrogen atmosphere and at room temperature.

1.2. Results and discussion

Fig. 1 shows the current density versus electric field of 100 nm thick films of neat MoO_x, neat NPB, and MoO_x:NPB (50:50) mixture in vertical structures. Clearly, the current density at any given voltage is higher in case of the MoO_x:NPB (50:50) mixture than in case of the neat films, including the neat MoO_x film. This is different from the results reported by Matsushima et al. [10] and Ma et al. [17] where the conductivity of the doped film did not exceed that of the neat MoO_x films. The discrepancy might be attributed to the use of vertical structures, which cause I–V characteristics highly sensitive to any small or subtle variations among test samples (e.g. small variations in ITO and/or film quality). The I–V characteristics of a thin film are typically governed by both charge transport in the film bulk and charge injection at the interface of the film/electrode. Since in a vertical structure the current flow path is across the film thickness (~100 nm), the I–V behavior could be more strongly influenced by interfacial effects rather than by transport across the film, causing bulk conductivity effects to be much less pronounced. To eliminate this ambiguity, we use lateral structures that allow for a much longer current flow path (tens

of micrometers) in the thin film, thus making charge transport in the bulk more pronounced in the I–V characteristics. Fig. 2(a) shows I–V characteristics from a series of lateral test devices with a 100 nm thick MoO_x:NPB layer of different MoO_x concentrations, whereas Fig. 2(b) displays the current at 10 V in the devices versus MoO_x concentrations. The inset of Fig. 2(b) shows the schematic layer structure of these devices. In these devices, the current flow occurs from one Ag electrode to the other laterally across the 26 μm gap through the layer, under the applied bias. (Fig. 2(c) shows the same I–V data of Fig. 2(a) but in the form of current density versus electric field, assuming that the current density and electric field across a vertical cross section in the film in the gap region are uniform. As the level of uncertainty in this assumption is unknown, Fig. 2(c) is provided only to allow approximate comparisons with other data in the first order.) One can observe that all devices exhibit almost linear I–V characteristics over the voltage range of 0–20 V (see Fig. 2(a)), while the current amplitude varies significantly from 10^{−11} to 10^{−5} A, depending on MoO_x concentration. As the MoO_x content increases from 0% (i.e. neat NPB) to 50% (MoO_x:NPB of 50:50), the current increases from 2 × 10^{−11} A to 1 × 10^{−5} A at around 10 V, corresponding to almost six orders of magnitude increase in conductivity. Interestingly, the current starts to decrease on further increasing MoO_x content beyond 50%, and drops back to 2 × 10^{−10} A for MoO_x content 100% (i.e. neat MoO_x). The data reveals that at the optimum composition, the MoO_x:NPB (50:50) mixture demonstrates a conductivity that is almost five orders of magnitude higher than that of neat MoO_x.

The much higher conductivity demonstrated by the MoO_x:NPB mixture can be attributed to the formation of charge transfer complexes between MoO_x and the HTM [13], as reported before from absorption spectra of such mixtures [13,18,19]. UV–Vis absorption measurements on our films reveal the presence of a broad absorption band centered around 1400 nm in case of the mixtures, consistent with those earlier reports. The charge transfer can be expected to result in an increase in the concentration of “free” carriers, and hence facilitate conduction in the mixture. It is therefore not surprising that the conductivity of the MoO_x:NPB mixture reaches its maximum at 50:50 ratio.

While, in a lateral device, the changes in I–V with MoO_x concentration can be expected to mostly arise from changes in bulk conductivity of the mixture layer, it is still possible that variations in charge injection at the metal contacts, associated with variations in MoO_x concentration, affect the observations non-negligibly. Therefore, to investigate this possibility, we fabricate and test a set of devices that all have a 100 nm thick MoO_x:NPB(50:50) film, but with various gap sizes (25.4 μm, 38.1 μm and 50.8 μm). Fig. 3 shows the I–V characteristics of these devices, whereas the figure in the inset shows the corresponding resistance versus gap size trend. The linear correlation between the resistance and the gap size indicates that the I–V

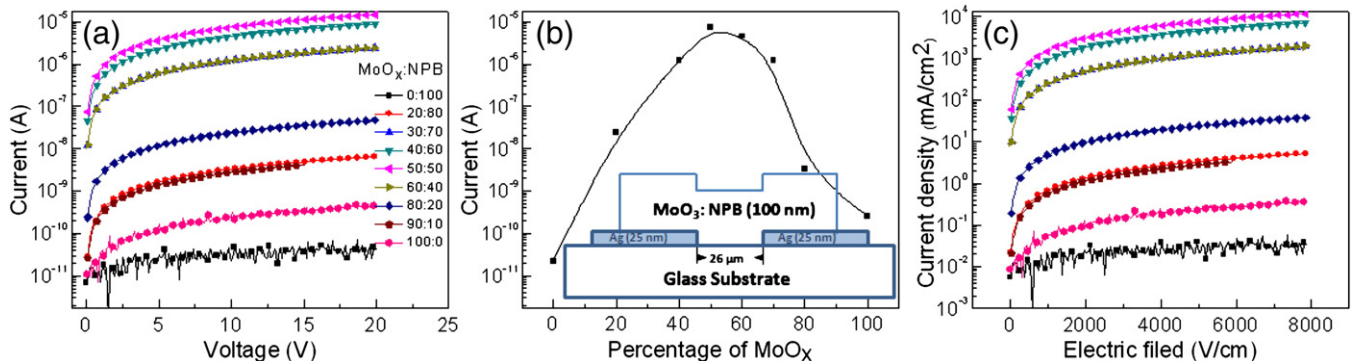


Fig. 2. (a) The I–V characteristics of MoO_x:NPB with various MoO_x (y%) concentrations. (b) The current of 100 nm MoO_x:NPB(ratio) films under 10 V in lateral structure as a function of MoO_x concentration (y). The inset of Fig. 2 (b) is the schematic layer structure of the lateral structure with 100 nm NPB and MoO_x mixture film. (c) The current density vs. electric field MoO_x:NPB with various MoO_x (y%) concentrations.

Download English Version:

<https://daneshyari.com/en/article/8036787>

Download Persian Version:

<https://daneshyari.com/article/8036787>

[Daneshyari.com](https://daneshyari.com)