Improved anode material for orange-dye as organic semiconductor

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We investigated the metal-semiconductor charge injection process to find the most suitable ohmic metal for Orange-Dye (OD) as organic semiconductor. For this purpose, different metal-semiconductor Schottky diodes such as (a) Au/OD/Al, (b) SnO_2/OD/Al, (c) Ni/OD/Al, and (d) Ga/OD/Al were fabricated and electrically characterized. It is observed that all Schottky diodes follow space charge limited model to define their charge transport mechanism and at the same time Ga/OD interface offered best electrical response, while Ni/OD interface offered lowest electrical responses. As, aluminum electrode and all other fabrication parameters are same for all Schottky diodes, therefore it is inferred that the improved electrical response for Ga/OD/Al Schottky is mainly due to Ga-OD interface. To compare, a simple relative charge injection-efficiency parameter (with respect to Ga) is calculated as 70, 32, 30 and 100% for Au, SnO_2, Ni, and Ga anode respectively. It is further observed that relative charge injection efficiency parameter is not a strong function of higher electric-field.

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1. Introduction

Organic semiconductor devices such as Organic-light-emitting diodes (OLED) have already reached at the stage of full-scale commercialization [1-3]. Despite the pronounced improvements in their optical efficiency, some of the fundamental features of both charge injection as well as charge transport process are not very clear and still being debated among different research groups [4-8].

Charge injection from metal electrode to organic semiconductor or vice-versa plays a vital role to define the efficiency of organic electronic devices. Under the influence of applied voltage, electrons and holes are injected from metal to organic semiconductor layer and are hoped randomly from one molecular chain to other molecular chain as bulk charge transport process inside the organic semiconductor to reach their respective electrode [9,10]. Generally, high work function metal injects holes from their Fermi level into the lowest unoccupied molecular orbitals (LUMO), while low work function metals inject electron from their Fermi level into the highest occupied molecular orbitals (HOMO) of any organic semiconductor layer [11].

For efficient electronic devices, it is very crucial to provide low resistance or ohmic contact from metal to organic layer to improve the electrical response of organic devices. In a single layer organic Schottky diode, the total current passing through the diode is either bulk limited, injection limited or combination of these two currents, depending on the ohmic or non-ohmic behavior of the metal-organic interface. Injection limited response is achieved when only metal-organic interface provides some restriction to the flow of charge carriers through the semiconductor. On the other-hand, for bulk limited response of metal-organic interface the only bulk semiconducting material provides the limitation to the flow of charge carriers through the semiconductor [12]. It is generally accepted that both these limiting responses can occur simultaneously for many organic semiconductors [12,13]. Now the question arises that which limiting process is dominated for a given metal-organic interface. It depends on many parameters such as organic-layer thickness, metal-organic interface barrier height, ambient temperature, applied voltage and can be roughly estimated through their measured current-voltage (I-V) characteristics.

In this study we used Orange Dye (OD) as organic semiconductor due to many reasons. Historically, OD is a colored powder with common application to pass-on color to other textiles, paper, leather substance just like as many other dyes. Recently, OD is also discovered as a novel *p*-type organic semiconductor material and showing great potential for many electronic and optoelectronic devices. OD has highly environmental stability and offers ease of synthesis specially for sensor applications [14-20]. The molecular structure of OD is shown in Fig. 1, while some physical information of OD is given in Table 1.

The metal-semiconductor, the energy barrier height is an important parameter and some-time used to compare the charge injection efficiency of different electrode to semiconductor with the help of Mott-Schottky model [21]. The Mott–Schottky model states that the energy barrier height between metal and semiconductor interface can be estimated by the difference between the semiconductor's electron affinity and metal work function. But unfortunately, the measurement of the energy barriers height itself for charge injection from metal to organic semiconductor is very challenging because of many reasons such as failure of the Mott–Schottky principle, lack of well-define Fermi-energy level, reactive surface bonds interaction and as well as the presence of very complex interfacial dipole for many organic and polymer semiconducting materials [22,23]. Therefore, to investigate the suitable metal electrode for OD for their improved electrical response we propose a very simple but innovative approach as discussed below in section 3.

In this study we investigated and compare the different electrode materials such as Al, Ni, SnO_2 and Ga and find out the most suitable electrode which gives relatively improved electrical response with respect to OD semiconductor.

Table 1. Some physical properties of OD

Technical Name:	3-[ethil[4-[(4-nitrophenyl)azo] phenyl] amino] propanenitrile
Conventional Name:	Orange Dye
Chemical Formula:	$C_{17}H_{17}N_5O_2$
Molecular Weight:	323.3536 (amu)
Density:	0.9 gm/cm^3
Melting Point:	170 ^oC
CAS RN:	31482-56-1

2. Experimental

The synthesis of the OD was described elsewhere [24], while the OD films were deposited in demineralized water from the 10% by weight solution and were grown at room temperature by using spin coating method at 300 rpm for 30 seconds over the top surface of Al pre-coated glass substrate, whereas other electrodes were deposited by vacuum evaporation method over OD surface. Optical examination showed that the OD films grown were homogeneous and the thicknesses of the polymer films were estimated in the range of 1 ± 0.15 µm. Although it is well-reported that OD is a *p*-type semiconductor just like as many other organic semiconductors, but by using hot-probe method it was re-confirmed that the grown films were *p*-type semiconductors. Fig. 1 shows cross-sectional view of the finished device. Among all other electrodes (Al, Ni, Au, Ga and SnO_2), Al has the lowest work function, so it can be justified that Al behaves as cathode and injects electrons into the *p*-type OD layer as compared to the other electrode. For this study all samples are electrically characterized through current-voltage characteristics (*I-V*) with temperature adjusting facilities. The *I-V* measurements were carried out in the temperature range from 30 to 70 ^oC with an estimated temperature error was found in the range of ± 0.5 ^oC.

In this study, all Schottky diodes (a) Au/OD/Al (b) Ni/OD/Al, (c) SnO_2/OD/Al, and (d) Ga/OD/Al were fabricated with same Al cathode and OD film thickness under same ambient room temperature and other processing conditions. With the help of electrical characterization, the relative charge injection efficiency of different electrodes was estimated and discussed to point out the most suitable anode for OD semiconductor.

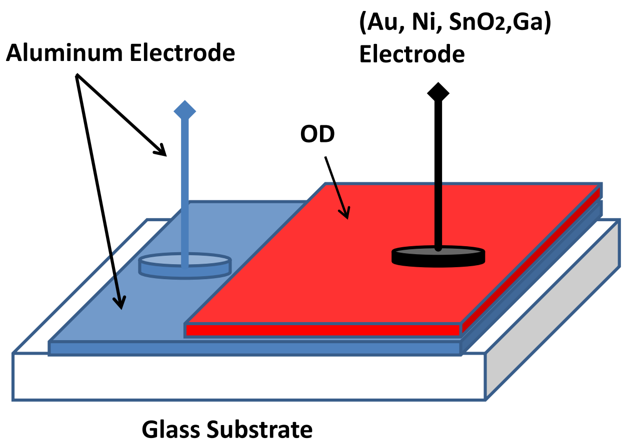

Fig. 1. A schematic cross-sectional view of Metal / OD/ Al Schottky diode. Where OD thin film deposited with a spin-coating method onto a precoated aluminum thin film on a glass substrate for electrical characterization

3. Results and discussion

The current-voltage characteristics of OD with Au, Ni, SnO_2 and gallium anode for devices (a) Au/OD/Al (b) Ni/OD/Al, (c) SnO_2/OD/Al, and (d) Ga/OD/Al as Schottky-diodes are shown in Fig. 2. It is observed that each Schottky -diode shows a typical non-linear rectifying behavior and current is sharply rises at higher electric field for all devices. At low electric field the energy of emitted holes is less than the anode-OD barrier height, therefore negligible current is observed for all devices till the threshold voltage. After threshold voltage the emitted holes easily surpass the anode-OD barrier height and start to rise sharply with increasing voltage due to the electric field induced reduction of anode-OD energy barrier height as reported by many research groups [25,26]. It can be perceived from the figure that better electrical responses among these devices is may be due to the improved interface behavior of Ga, Au, SnO_2 and Ni anode in respective order because these electrodes may offer the lowest energy barrier-height to highest energy barrier-height to the emission of holes inside OD layer respectively.

Charge transport process of holes for organic semiconductor is either injection or bulk limited transport, but it is a direct function of ambient temperature. Hence, we measured the current-voltage response for all devices (a) Au/OD/Al (b) Ni/OD/Al, (c) SnO_2/OD/Al, and (d) Ga/OD/Al respectively at 50, 60 and 70 ^oC. To determine the nature of bulk charge transport mechanism if we plot the logarithmic current vs logarithmic voltage, a linear relation is obtained at higher electric field, which shows that all devices follow space charge limited current especially at higher electric field. The SCL current (J_{SCL}) can be defined by the Mott-Gunney law as [27,28],

$$J_{SCL} = \frac{9}{8}\varepsilon\varepsilon_o\mu\frac{V^2}{L^3} \tag{1}$$

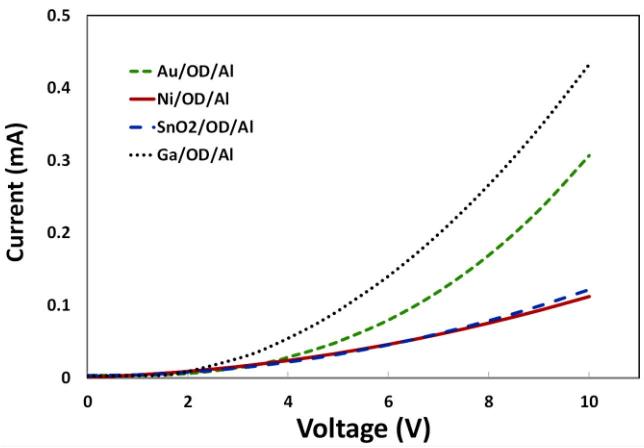

Fig. 2. Current-Voltage characteristics of (a) Au/OD/Al, (b) Ni/OD/Al, (c) SnO_2/OD/Al, (d) Ga/OD/Al (color online)

where ε,ε_o are the relative and absolute dielectric constant of OD, V is the applied voltage, L is the thickness of OD layer. Fig. 4 shows the logarithmic voltage and current for all devices at 60 ^{o}C, which clearly represents that despite the charge injection limited current, bulk region of all devices still follows space charge limited current. Nearly similar response is also observed for all devices at 50, 70 and 80 ^{o}C, but for simplicity here we show the space-charge response for all devices only for 60 ^{o}C. From equation (1) all parameters such as ε,$\varepsilon_{o,}$ μ, V and L are constant for each diode, so it can be estimated that in our case the total current is attributed to the combination of both bulk and interface injection limited current [29].

$$J_{TOT} = J_{SCLC} + J_{ILC} \tag{2}$$

while, the variation in current-voltage characteristics due to different anode as shown in Fig. 3 is not due to the bulk space charge limited but due to anode-OD interface limited injection current, because all bulk related parameters as well as Al cathode is common for all Schottky diodes. Now, the question arises that despite of injection limited anode-OD interface, why bulk space-charge limited current behavior is observed. For this purpose, we calculated the mobility from equation 1 and plotted as a function of temperature shown in Fig. 4. We observed a very small mobility (close to 0.001 cm^2/V. sec). So, we can easily conclude that in the presence of injection limited anode-OD interface the very low density of charge carriers is injected from anode and these charges are hopped inside the bulk region of OD with very small mobility. Compared to the rate of charge injection to the rate of charge transport from one location to the other location is so small that space charge is started to build-up throughout the bulk OD region and henceforward all diodes obey Mott-Gunney space-charge model for their bulk OD region. As bulk OD film has same thickness and other parameters for all devices, therefore difference in the current at the same voltage from one device can be co-related to the charge-injection response of the devices. Fig. 2 shows that Ni anode offered the lowest current for charge injection to the OD thin to the improved anode film. On the other words, we can say that Nickel anode offered highest injection limited barrier to the OD layer, Ga anode offered lowest injection limited barrier to the OD layer. So, we define relative charge injection efficiency of each anode with respect to Ga anode at applied electric field 5 volts and ambient room temperature environment as

$$\eta_{anode}\,(\%) = \frac{I_{anode}}{I_{Ga}}\; X\; 100 \tag{3}$$

where I_{anode} and I_{Ga} are the current of OD with any anode and Ga electrode at same voltage and temperature respectively. Table 2 shows the injection efficiency of different anode with respect to Ga anode, where Ga anode shows the highest relative injection efficiency among the given electrode to the OD layer at room temperature. The relative charge injection efficiency of both anode Ni and SnO_2 is very low but nearly same to each other. While, Au offered the second highest relative charge injection efficiency after Ga Anode.

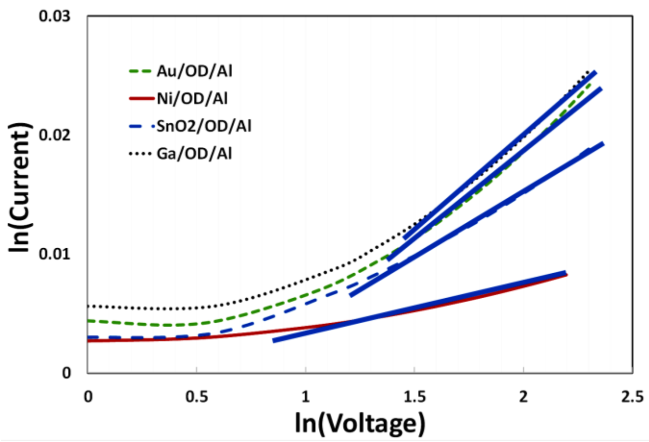

Fig. 3. Ln(Current) vs ln(Voltage) characteristics of (a) Au/OD/Al, (b) Ni/OD/Al, (c) SnO_2/OD/Al, (d) Ga/OD/Al to verify the space charge limited current in the bulk region of OD film (color online)

Table 2. Relative injection efficiency (η_{anode}) of different anode to the OD layer

Anode	Cathode	Diode	η_{anode}
Au	Al	Au/OD/Al	70%
Ni	Al	Ni/OD/Al	30%
SnO2	Al	SnO2/OD/Al	32%
Ga	Al	Ga/OD/Al	100%

The Fig. 5 shows the behavior of relative charge injection efficacy as a function of applied electric field for all devices, which evidently demonstrates that the relative charge injection efficiency does not change sharply as a function of applied voltage. For both SnO_2/OD/Al and Ni/OD/Al the relative charge injection efficiency is slightly (negligible) decreasing with applied voltage, while Au/OD/Al the relative charge injection efficiency is some extent increasing with applied voltage. The relative charge injection efficiency depends on the rate of increasing current at higher electric field and Au/OD and Ga/OD shows similar current growing trend as compared to SnO_2/OD and Ni/OD interfaces, therefore Au/OD interface displays slightly increasing while SnO_2/OD and Ni/OD interfaces demonstrate decreasing trends as a function of higher electric field as observed in Fig. 6. So, it can be acceptable that relative charge injection efficiency is not very strong function of the applied electric voltage.

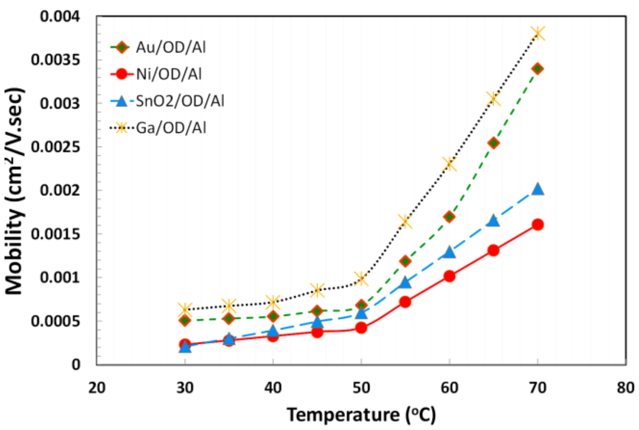

Fig. 4. Mobility of (a) Au/OD/Al, (b) Ni/OD/Al, (c) SnO_2/OD/Al, (d) Ga/OD/Al calculated from Mott-Gunny space - charge limited current model (equation 1) (color online)

4. Conclusion

In this study, we investigated the most suitable anode metal for OD among most commonly reported electrodes material such as Au, SnO_2, Ni and Ga metal electrodes. For this purpose, four different Schottky diodes were fabricated as (a) Au/OD/Al, (b) SnO_2/OD/Al, (c) Ni/OD/Al, (d) Ga/OD/Al at the same time, under similar environmental and processing conditions with same Al metal as cathode, the only varying parameter is anode electrode itself. From electrical characterization the variation of current-voltage characteristics is observed for all diodes and Ga/OD/Al offered highest, while Ni/OD/Al lowest current response. It is observed that all diodes follow space charge limited current model for bulk OD region mainly due to very low mobility. As all space charge and process parameters are same for each diode, so we inferred the improved electrical response due to enhanced anode-polymer interface. The metal-polymer interface barrier height is complex in nature to quantify; therefore, we introduce a simple relative charge injection efficiency as percentage ratio between diode current to the highest diode current (here Ga/OD/Al in our case) at fixed voltage. We determine relative charge injection efficiency as 70, 32, 30 and 100% for diodes a) Au/OD/Al, b) SnO_2/OD/Al, c) Ni/OD/Al, d) Ga/OD/Al respectively. It is also observed that relative charge injection efficiency is constant or slightly varied (increased/decrease response) at higher applied voltage. So relative charge injection efficiency is not a strong function of the applied electric field.

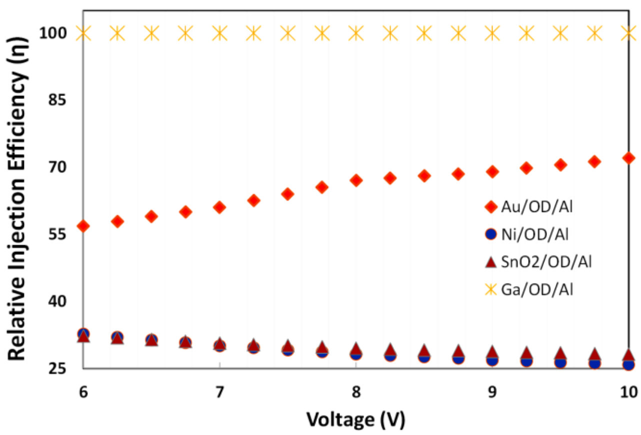

Fig. 5. Relative charge injection efficiency vs Voltage characteristics of (a) Au/OD/Al, (b) Ni/OD/Al, (c) SnO_2/OD/Al at room temperature (color online)

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