

# Protonated metal-oxide electrodes for organic light emitting diodes

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## Abstract

Protonation of the indium tin oxide (ITO) electrode surface by nitric acid vapor gives rise to an ionic double layer producing an important increase in the effective electrode workfunction. This shift of  $\sim 0.8$  eV can be determined from the photoresponse of single layer diodes consisting of tris (8-hydroxyquinoline) aluminium (Alq) sandwiched between protonated ITO and aluminium electrodes. Due to the chemical treatment, the contact between the protonated hole injecting oxide electrode and Alq becomes ohmic. Under an applied electric field, the efficient injection of holes produces a positive space charge in the organic layer which enhances the emission of electrons from the cathode. © 1998 Elsevier Science B.V.

Due to their potential technological applications, organic material-based electroluminescent devices (OLEDs) have gained much attention in the last decade. Thereby tris (8-hydroxyquinoline) aluminium (Alq) has been proven to form highly luminescent stable films which can be used in the construction of reliable OLEDs [1]. In order to obtain high photon to current efficiencies, it is necessary to balance electron and hole currents through the device. The current and light emission characteristics are determined both by the injection barriers at the various interfaces and the charge carrier mobility of holes and electrons, respectively. It has been suggested that the injection of electrons is mainly determined by the workfunction of the cathode, usually consisting of a

metal [2]. For the injection of holes, indium tin oxide (ITO) is commonly used. It has a workfunction of about 4.8 eV which allows efficient injection of positive carriers into numerous organic solids composed of molecules such as diamines or polymers such as poly-(para-phenylene-vinylene) [2,3].

It is, however, difficult to inject holes from ITO into molecules with a high oxidation potential such as Alq. In a previous work we have shown that the injection barrier can be lowered by grafting molecules with oriented dipoles at the oxide surface [4,5]. In this case, an interfacial field is created by the adsorbates, modifying the workfunction of the derivatized electrode.

If polymers are doped with ions, the latter will drift towards the electrodes when an electric field is applied through the device. Similarly to an electrochemical electrode in solution the ionic layer at the device electrode will produce an interfacial field that

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modifies the effective workfunction (as the effective workfunction we mean the workfunction of the electrode including the ionic surface layer). It has been shown that injection barriers can be reduced considerably this way [6]. Efficient solid polymer light emitting electrochemical cells have been conceived that consist of a mixture of an emitting polymer and an ion conducting polymer [7].

While numerous works have reported on the metal-organic interface [8,9], only little is known of the nature of the interface between the organic bulk material and an oxide electrode. Adsorption of molecules can involve all kinds of chemical bonds ranging from Van der Waals bonds, H-bonds or ionic bonds to covalent bonds [10,11]. Specific adsorption of ions to ionic surfaces including oxides is well known in solution electrochemistry [12]. In particular, protons can also have a high electrode affinity and thereby give rise to a chemical potential shift across the interface. A well known application of this effect is the pH meter which is based on a glass electrode with high proton selectivity. Theoretical calculations suggest that covalent effects are governing the acido-basic properties of oxide surfaces [13]. An ionic oxide material such as ITO is also expected to show proton affinity due to hydroxyl groups or anionic oxygen sites at the surface.

In this work we report on a method to protonate the ITO surface by a nonhalogen acid. Unlike other studies, where concentrated halogen acid etchants were used to modify the surface roughness of the electrode [14], we were interested in the effect of chemically adsorbed nitric acid. In analogy to the pH electrode in solution, we have attempted to build a solid ionic double layer at the surface consisting of adsorbed protons and negative counterions. The negative counterions of the acid which are necessary to maintain charge neutrality would have no other choice but to align on top of the adsorbed protons, if they are chosen big enough. Fig. 1 shows a schematic view of such an ionic double layer that is in contact with the organic material.

In order to investigate the physical properties of such an electrode in optoelectronic, solid devices, we have built single layer organic electroluminescent devices. Thereby we have found important differences in the photoresponse, current–voltage and light emission characteristics when using the chemically

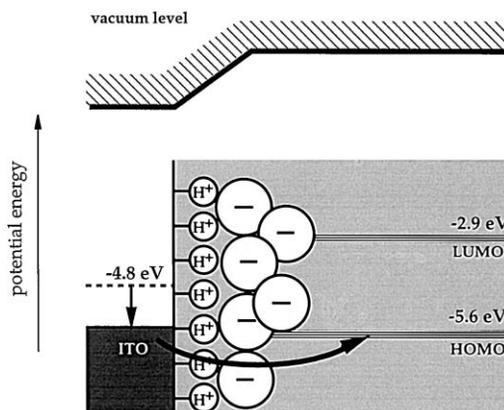


Fig. 1. Schematic view of a protonated oxide electrode in contact with an Alq film. The lowest unoccupied and highest occupied molecular orbitals are indicated by horizontal lines. The effect of the ionic double layer on the effective ITO workfunction is also indicated in the picture.

modified ITO electrode instead of a conventional one.

In order to obtain reproducible experimental conditions, the ITO conducting glass (Balzers,  $50 \Omega/\square$ ) was first cleaned by ultrasonic agitation in ethanol and acetone followed by mechanical scrubbing in distilled water using a detergent. The metal-oxide substrate was then cleaned in an ultrasonic bath consisting of a water solution of the same detergent followed by several rinsing steps in doubly distilled water. After drying, the conducting glass was transferred into a vacuum chamber and ion bombarded in an argon atmosphere at a pressure of  $8 \times 10^{-2}$  Torr using low rf power. It has been shown that a gentle plasma cleaning of this kind does not affect the ITO surface, either chemically or from a morphological point of view [15]. After the plasma cleaning, the substrates were again immersed in distilled water to hydroxylate the surface. Finally the dried substrates were briefly exposed to the vapor over a concentrated (65% wt) nitric acid solution. (An alternative way of acid adsorption consists of soaking the substrates for 2 min in water at a pH of 3 using  $\text{HNO}_3$  to adjust the pH. The substrates were then dried with an air gun). In the following text we will refer to this electrode as the protonated electrode  $\text{ITO-H}^+$ . For comparison ITO electrodes were used where the acid treatment has been omitted. We have called them untreated ITO electrodes in the following.

The chemically treated substrates were used to construct organic devices consisting of a single organic layer terminated by an aluminium electrode. In this work the organic material consisted of the well known emitter Alq which was supplied by Aldrich and used without further purification. 140 nm thick Alq films were vacuum deposited from a tungsten crucible at a pressure of about  $5 \times 10^{-7}$  Torr and a rate of 0.5 Å/s. In the same pump down, a 50 nm thick aluminium layer was evaporated from another tungsten crucible. The source to substrate distance was about 30 cm for the deposition of both Alq and the metal. For comparison, we have prepared a device similar to the above type in which the protonated ITO electrode was replaced by a gold electrode.

In order to investigate the charge transport characteristics of these single layer devices, we have constructed electron-only and hole-only devices, too. The symmetric electron-only device was based on a 140 nm thick Alq layer sandwiched between two aluminium electrodes. Again the sandwich diode was constructed in a single pump down. First, a 40 nm thick aluminium layer was deposited on glass, followed by a 140 nm thick Alq layer and a 50 nm thick top electrode. The hole-only device consisted of a protonated ITO electrode, a 140 nm thick Alq layer and a gold top electrode. In order to avoid thermal degradation during the vacuum deposition of gold, the substrate was cooled to approximately  $-100$  °C. All thicknesses were measured during vacuum deposition using a quartz thickness monitor and were confirmed by a second measurement using a Tencor Alpha-Step 500 profilometer. The surface geometry of all the diodes used in this work consisted of squares of either 4 mm<sup>2</sup> or 16 mm<sup>2</sup>.

We used a Keithley 237 source measure unit connected to a personal computer to measure the current–voltage characteristics. Light emission intensities were measured in a well defined geometrical arrangement using a calibrated Graseby Optronics 247 photodiode connected to a Keithley 2000 multimeter. For the photoresponse measurements we used an unfiltered tungsten–halogen lamp providing a white light irradiation intensity of 10 mW/cm<sup>2</sup> to 20 mW/cm<sup>2</sup>. All the electric and optic measurements were carried out in an inert argon atmosphere.

As mentioned above the effective workfunction of

an electrode is a critical parameter in the construction of organic LEDs. In order to estimate the effective workfunction of the protonated ITO electrode (ITO–H<sup>+</sup>), it is appropriate to make a comparison between different reference electrodes. This can be achieved by measuring the built-in potential between two kinds of electrodes. Bare (unprotonated) ITO has a literature value of about 4.8 eV but we have found that its effective workfunction is dependent on the way of preparation. The quality of the distilled water, for example, is of crucial importance. Due to this uncertainty we attached more importance to gold or aluminium as a reference material for the workfunction in our devices.

When a single layer device sandwiched between two asymmetric electrodes is short-circuited, an electric field appears in the layer. Under illumination, this electric field is able to separate holes and electrons, which is the principle used in photovoltaic devices. Here we used this effect to measure the photocurrent of the device, from which we infer the built-in potential,  $V_{bi}$ . The method consists of taking current–voltage characteristics at low field under illumination. The crossover of the dark and illuminated curve yields  $V_{bi}$  [16,17]. The procedure has been applied to several known electrode combinations and the difference in electrode workfunctions was obtained with reasonable accuracy independently of the organic layer [18]. We applied a tungsten halogen lamp for illumination at two different white light intensities of 16 mW/cm<sup>2</sup> and 17 mW/cm<sup>2</sup>. The photocurrent characteristics for the different diodes are shown in Fig. 2. For all diodes, the crossover of both curves with the dark current–voltage characteristics occurs at the same voltage, thus indicating saturation conditions.

The symmetric device consisting of an Alq layer sandwiched between two aluminium electrodes yields an open-circuit potential of  $0 \pm 0.1$  V which has to be expected for two identical electrodes. For the device with a gold and an aluminium electrode we obtain a voltage of  $1 \pm 0.1$  V with the positive bias applied to gold. This value is in good agreement with the difference between the literature workfunctions of gold (5.1 eV) and aluminium (4.2 eV). A diode sandwiched between aluminium and untreated ITO gives a photovoltage of  $0.6 \pm 0.2$  V when the positive bias is applied to ITO, which is again consistent

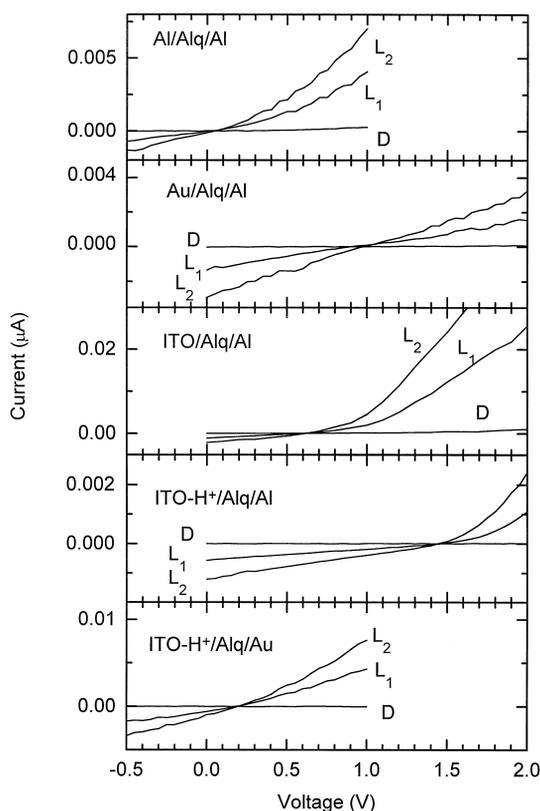


Fig. 2. Current–voltage characteristics under saturated white light illumination at  $16 \text{ mW/cm}^2$  (L1) and  $17 \text{ mW/cm}^2$  (L2). The crossing with the dark current–voltage curve (D) yields the built-in potential  $V_{bi}$  of the device. All four devices consist of 140 nm thick Alq layers that are sandwiched between two electrodes. ITO and ITO–H<sup>+</sup> stands for the untreated and protonated indium tin oxide electrode, respectively. Al and Au are used for aluminium and gold, respectively.

with the difference between the literature values of the ITO and aluminium workfunctions. In the case of a diode consisting of the protonated ITO–H<sup>+</sup> and an aluminium electrode, the positive bias was applied to ITO–H<sup>+</sup>. Strikingly, the photovoltage is as high as  $1.5 \pm 0.1 \text{ V}$  which is more than twice the voltage that is obtained with an untreated electrode. This was indeed what we expected from an electrode with high proton affinity. Since we used nitric acid to protonate the oxide surface, the much larger NO<sub>3</sub><sup>−</sup> anions are susceptible to aligning on top of the adsorbed protons such that charge neutrality is preserved (see Fig. 1). This ionic double layer now creates an interfacial electric field that can yield a high increase of the effective workfunction if the

surface density of protons is important. Other chemical surface modifications, such as those encountered in etching reactions under drastic conditions [19], could also give rise to an interfacial field but are unlikely to occur under the low acid concentrations used in this work.

Given that the ITO–H<sup>+</sup> electrode is in direct contact with the organic material, the highest possible change in the photovoltage will be limited by the ionization potential of Alq. If the effective electrode workfunction would be higher than the ionization potential of the organic semiconductor, charge would simply be transferred from one to the other in order to equalize the Fermi levels. From the photovoltage of 1.5 V and taking an aluminium workfunction of 4.2 eV we get a value of 5.7 eV for the ITO–H<sup>+</sup> effective workfunction. This value is about equal to the oxidation potential of Alq ( $E_{\text{HOMO}} = -5.6 \text{ eV}$  versus vacuum) [20] suggesting that ITO–H<sup>+</sup> forms an ohmic contact with Alq. We have also investigated diodes based on ITO–H<sup>+</sup> and gold contacts taking ITO–H<sup>+</sup> to apply the positive bias. The photovoltage of  $0.2 \pm 0.1 \text{ V}$  shows the right trend underlining that ITO–H<sup>+</sup> has a higher effective workfunction than gold.

Alq is well known as an electron transporting layer into which it is difficult to inject holes. It is commonly used in conjunction with a hole transporting layer such as tri-phenyl-diamine which also has the effect of blocking electrons at the organic interface. Taking advantage of the extraordinarily high effective workfunction of ITO–H<sup>+</sup> that gives rise to ohmic injection into Alq, we are now able to study the effect of hole injection into single layer Alq devices in absence of any hole transporting materials.

Fig. 3 shows the current voltage characteristics of the different devices, all consisting of a 140 nm thick single Alq layer. Clearly the lowest current onset-voltage is obtained for the diode with an ITO–H<sup>+</sup> anode and an aluminium cathode (referred to as ITO–H<sup>+</sup>/Alq/Al in the following). The inset shows a logarithmic plot of the same diode under forward and reverse bias. At high electric fields the rectification ratio between the two currents attains 8 orders of magnitude. This shows that the low onset-voltage is not due to ion migration under the applied field, but to a permanent ionic double layer formed by the

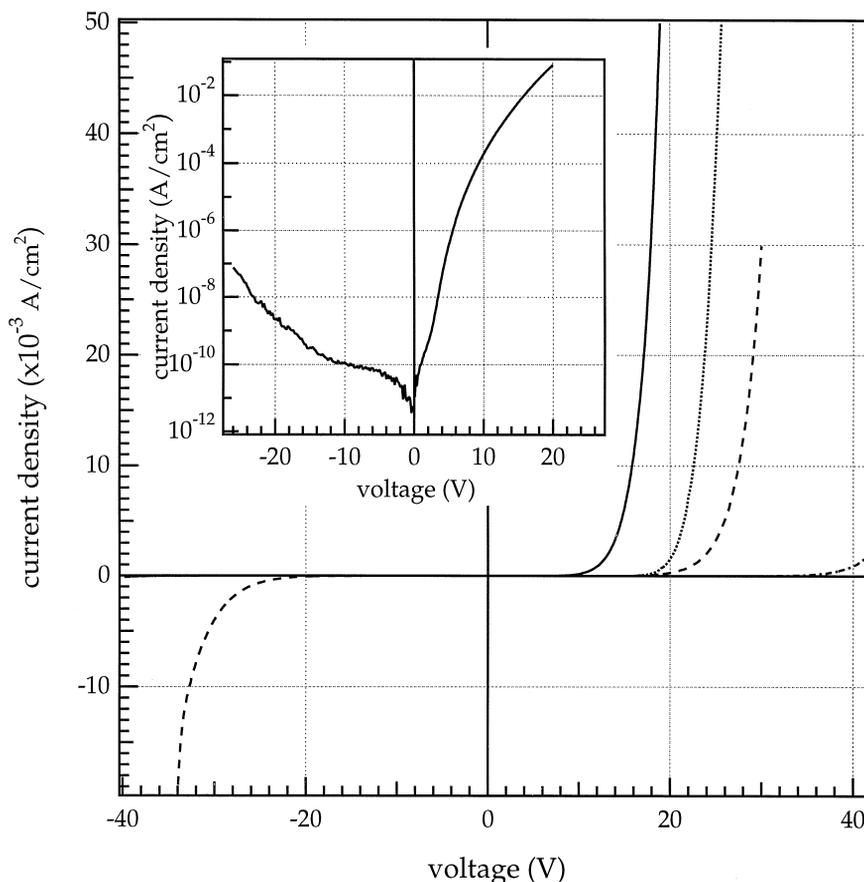


Fig. 3. Current–voltage characteristics of 140 nm thick Alq layers sandwiched between a ITO–H<sup>+</sup> and an aluminium electrode (solid line), a gold and an aluminium electrode (dots), two aluminium electrodes (dashes) and an ITO–H<sup>+</sup> and a gold electrode (dash-dotted line). The inset shows a logarithmic plot of the ITO–H<sup>+</sup>/Alq/Al device under forward (positive) and reverse (negative) bias.

protonation. The diode with a gold anode and an aluminium cathode has a higher onset potential than the same diode using an ITO–H<sup>+</sup> anode. Contrary to the frequently used double layer devices where hole injection seems to have little influence on the device characteristics [21], the workfunction of the anode which determines the holeinjection efficiency in this type of construction considerably influences the current–voltage characteristics.

In order to get more insight into the current–voltage characteristics of these bipolar single layer Alq devices, we have also investigated the homopolar devices. In Fig. 4, a double logarithmic plot shows the current–voltage characteristics of the homopolar and the bipolar devices. The hole-only and electron-only devices consist of an ITO–H<sup>+</sup>/Alq/Au and an

Al/Alq/Al layered structure, respectively. The difference of about three orders of magnitude between the two currents is consistent with the difference in carrier mobility between electrons and holes. In the bipolar device consisting of a ITO–H<sup>+</sup>/Alq/Al layered structure, the current is again increased by three orders of magnitude. The low onset current in the ITO–H<sup>+</sup>/Alq/Al device cannot be explained by the addition of a high hole current through the device since the hole current of the monopolar device ITO–H<sup>+</sup>/Alq/Au is about six orders of magnitude smaller at a voltage of 20 V. In fact, the mobility of holes is low. Values ranging from 10<sup>–8</sup> cm<sup>2</sup>/Vs to 10<sup>–6</sup> cm<sup>2</sup>/Vs have been reported [22,23]. The mobility of electrons, however, has been reported to be higher by about two orders of magnitude [24]. Given the

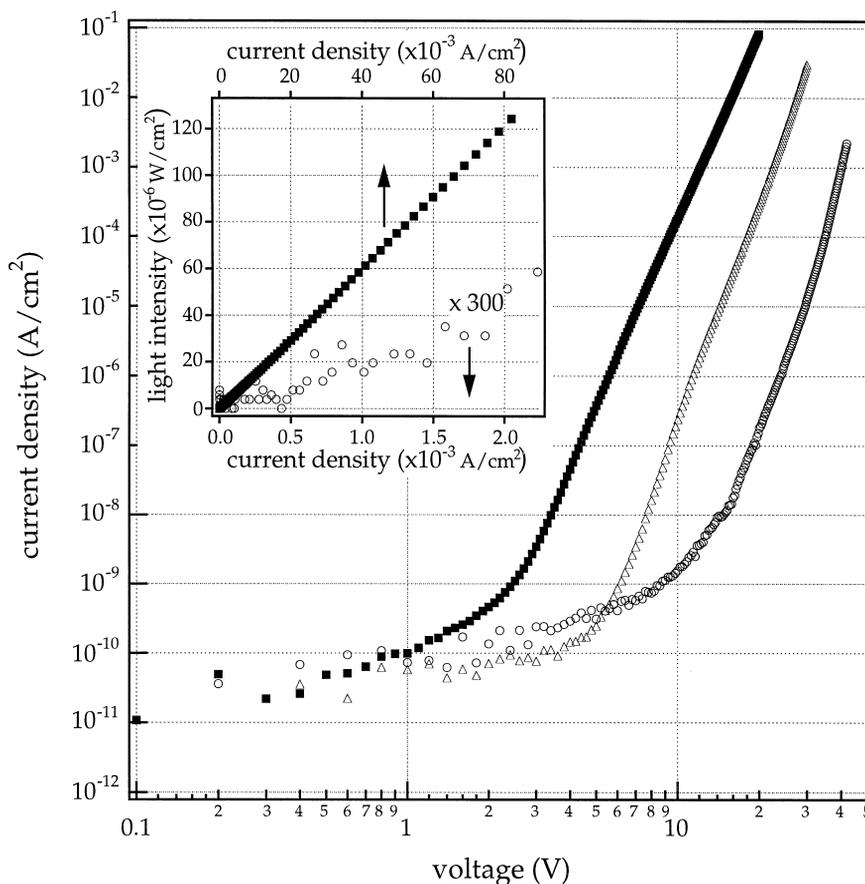


Fig. 4. Double logarithmic plot of the current–voltage characteristics of the “hole-only” device ITO–H<sup>+</sup>/Alq/Au (open circles), the electron-only device Al/Alq/Al (open triangles) as well as the bipolar device ITO–H<sup>+</sup>/Alq/Al (full squares). The inset shows the brightness-current characteristics of the same devices.

important difference between the mobilities of the two charge carriers, we arrive at the conclusion that the space charge in the organic film will be dominated by the positive charges with a high density of holes close to the ITO–H<sup>+</sup> electrode where ohmic injection occurs. In order to produce the important change in the onset potential, the current of the mobile carriers, i.e. the electrons has to be enhanced in some way. Therefore we argue some density of holes through the device must exist which attracts the electrons from the cathode. In other terms, the positive space charge gives rise to a supplementary electric field at the cathode that lowers the injection barrier for electrons. Further evidence will be given below using the emission characteristics of the devices.

The light emission characteristics are shown in the inset of Fig. 4. As could be expected, the electron-only device consisting of two aluminium contacts shows no light emission. Astonishingly, light emission is observed in the “hole only” device consisting of an ITO–H<sup>+</sup> anode and a gold cathode above an applied voltage of 40 V. It is surprising that gold is able to inject electrons into the LUMO of Alq ( $E_{\text{LUMO}} = -2.9$  eV versus vacuum [20]) although it has to overcome a huge energy barrier. Again the above interpretation can be invoked. Under a certain applied field, a positive space charge is built by the low mobility carriers that induces a high enough field at the gold electrode such that electrons can be injected.

For the ITO–H<sup>+</sup>/Alq/Al device, a quantum effi-

ciency of 0.075% was obtained at 20 V. This means that the approximate photon current emitted at this voltage is about  $6 \times 10^{-5} \text{ s}^{-1} \text{ cm}^{-2}$ . Given the fluorescence quantum yield of 10 % for an Alq film, [25] we arrive at a lower estimate of  $6 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-2}$  for the number of recombinations. This number is almost four orders of magnitude higher than the hole current of  $1.8 \times 10^{-7} \text{ A cm}^{-2}$  in the ITO–H<sup>+</sup>/Alq/Au device, measured at an applied voltage of 20 V. Since the recombination zone has been found to lie close to the hole injecting interface [25], we argue that the holes emitted from the protonated anode only have to travel a short way until they recombine with an electron. In this simplified picture the major contribution to the current in the bipolar device comes from the electrons traveling through the organic layer. A detailed description would involve a space charge limited current calculation taking into account carrier recombination [26]. From these findings we conclude that the recombination zone is likely to be close to the protonated anode such that holes which recombine only have to travel a short way. This view is consistent with other experimental findings in the literature. It also means that the major contribution to the current in the bipolar device is coming from the electrons traveling through the organic layer.

In conclusion, we have found that the saturated photovoltage method is convenient in determining the workfunction differences between the two electrodes of a single layer device. Using this method, we have demonstrated that an ionic double layer can be constructed at the oxide surface. Such ionic double layers could be a promising approach to tune the effective workfunction of oxide electrodes such that ohmic injection of carriers is attained. In addition to the energy barriers we also found that space charge affects charge carrier injection.

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