Interface dipole formation between GaMnAs and organic material

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Abstract. The interface band alignment between GaMnAs and organic material was investigated by current transport measurement in hole only devices with GaMnAs/NPB/Al structure. The current density – voltage ($J$-$V$) curves were measured and numerical simulations performed on this device structure yielded the hole injection barrier between GaMnAs and NPB to be 0.77 eV. A vacuum level shift at GaMnAs/NPB interface was deduced as 0.54 eV, indicating a dipole layer across the interface. We attributed the vacuum level shift to the charge transfer across the interface.

1. Introduction

Organic semiconductors have attracted considerable interest for their successful application in organic light emitting diodes and organic thin film transistors [1,2]. Recently, with the development of spintronics, organic semiconductors have been utilized as efficient spin transport layers due to their weaker spin-orbit coupling and hyperfine interaction, which render longer spin lifetime and spin diffusion length than those in inorganic materials [3]. Experimentally, spin valve devices based on tris(8-hydroxyquinoline) aluminium (Alq3) have been studied and spin diffusion length up to hundreds of nanometers at low temperature has been reported [4]. Theoretically, the spin dependent carrier injection and transport with respect to different contact resistances at the metal/organic interface have been calculated [5].

To achieve the spin injection into the organic semiconductor, carriers in the electrode must be highly spin-polarized. Ferromagnetic metals [6] and semimetals [7] have been used in previous studies. However, so far no report has been seen utilizing the ferromagnetic semiconductor GaMnAs as the spin-polarized carrier injection electrode. Ferromagnetic GaMnAs has very high spin polarization for holes in valence band at temperatures below its Curie-temperature [8]. In addition, GaMnAs may provide a better resistance match at the electrode/organic interface in comparison with ferromagnetic
metal/organic interface. This in turn leads to higher spin injection efficiency [9]. Thus, GaMnAs is a good candidate for hole spin injection electrode in organic spin based devices. In this paper, we investigated the interface formation between GaMnAs and \( N,N'\text{-diphenyl-N,N'\text{-bis(1-naphthyl)(1,1'\text{-biphenyl)-4,4'}\text{-diamine}} \) (NPB), a prototypical organic hole transporting material. Hole only devices with GaMnAs/NPB/Al sandwiched structure were fabricated. Current density – voltage (\( J-V \)) measurement were performed on these devices. Interface band alignment between GaMnAs and NPB was extracted by numerical simulation of the measured \( J-V \) curves to reveal the potential application of GaMnAs as a hole spin injector in NPB based organic devices.

2. Experiments

Ferromagnetic GaMnAs thin films with nominal Mn concentration of 5% and thickness of 20 nm were grown at 250 °C in a Riber 32 MBE system on (001) semi-insulating GaAs (SI-GaAs) substrates [10]. Post-grown annealing was performed in nitrogen atmosphere at 260 °C for 1 hour to enhance the hole concentration and the ferromagnetism of GaMnAs [11]. The curie temperature of the annealed GaMnAs was 103 K.

The device structure for \( J-V \) measurement is schematically shown in figure 1. The GaMnAs thin films were patterned into stripes with standard photolithography process, and etched in diluted HCl solution to produce Ga-Cl terminated surface [12], which is stable in air for at least 1 hour, long enough for the sample transfer [13]. NPB films of 70nm and Al of 60 nm were thermally evaporated onto the patterned substrates using shadow masks in an Edwards Auto 306 system. The device area was 400 \( \text{m} \times 500 \text{m} \). After deposition, the devices were transferred into a vacuum chamber where \( J-V \) curves were measured at room temperature using an HP 4155A semiconductor parameter analyzer.

![Figure 1](image.jpg)

Figure 1. (Color online) a schematic device structure for \( J-V \) measurements; GaMnAs is the anode and Al is the cathode.

3. Numerical model

Numerical simulations of the \( J-V \) curves have been performed using the hole injection barrier between GaMnAs and NPB interface as the fitting parameter. The theoretical models are based on the injection limited current (ILC) model [14,15] and the space charge limited current (SCLC) model [16,17]. The current continuity equation, Poisson’s equation, and the drift-diffusion equation are used to describe the charge transport.

We note that the electron injection barrier at the cathode interface (Al/NPB) is as high as 1.75 eV which is too large for an effective electron injection via Al/NPB interface within the bias range studied [18]. Unipolar device model is therefore constructed. The vacuum level shift at interfaces is included in the simulation. At NPB/Al interface, the vacuum level shift \( \Delta_2 \) is taken to be 0.45 eV [18]. The vacuum level shift at the GaMnAs/NPB interface is related to the hole injection barrier \( \phi_h \) (at zero bias) by:

\[
\Delta_1 = I_{\text{GaMnAs}} + \phi_h - I_{\text{NPB}}
\]

where \( I_{\text{GaMnAs}} \) and \( I_{\text{NPB}} \) are the ionization energy of GaMnAs and NPB, respectively. The ionization energy of GaMnAs \( I_{\text{GaMnAs}} \) is 5.27 eV, taking into account the broadening of the Mn impurity band and the merge of it with GaMnAs valence band [19]. The ionization of NPB is taken as 5.5 eV [20,21]. GaMnAs Fermi energy is assumed to be aligned with its valence band top due to its high doping level.
In the space charge limited conduction, Ohmic contact is assumed with the boundary condition \[16\]:

\[ p(0) = p_0 \tag{2} \]

where \( p(0) \) is the hole carrier density at the GaMnAs/NPB interface, and \( p_0 \) is the effective hole density of states in NPB highest occupied molecular orbital (HOMO).

4. Results and discussion

A typical \( J-V \) curve measured on GaMnAs/NPB/Al device is shown in figure 2 in semi-logarithmic scale, together with the simulated results by different models. By comparison, the injection limited model with the hole injection barrier of 0.77 eV at GaMnAs/NPB interface best fits the measured curve. The fact that the measured current density is much less than the current density predicted by the space charge limited model implies that the current transport of GaMnAs/NPB/Al device is limited by the interface injection. The discrepancy between the measured and the calculated \( J-V \) curve at lower voltage range (0 to 6 V) is possibly due to the Ohmic conduction before effective injection starts \[16\]. With the extracted hole injection barrier at GaMnAs/NPB interface, the vacuum level shift can be further calculated by equation (1) to be 0.54 eV. The calculated injection barrier and the vacuum level shift agree well with our UPS results discussed elsewhere \[22\].

![Figure 2](image_url)

**Figure 2.** (Color online) \( J-V \) curve measured (black open circle) and simulated by space charge limited model (red dash dot-dotted) and by injection limited model with 0.78 eV, 0.77 eV and 0.76 eV hole injection barriers at the interface (red dashed, blue solid, and black dotted, respectively).

Based on the simulation of the \( J-V \) measurement, the band alignment diagram at GaMnAs/NPB interface is schematically shown in figure 3, where the injection barrier calculated is represented as the band offset between the valence edge of GaMnAs and the HOMO edge of NPB, which is actually independent of the Fermi level position. The band bending at the surface of GaMnAs \[22\] is not shown for simplicity. The downward shift of the NPB vacuum level indicates a dipole layer as shown by red mark. This vacuum level shift is generally observed at metal/organic and semiconductor/organic interface, though the exact origin of the shift is not conclusive so far \[23-26\]. However, one theory based on the metal induced gap states have recently been used extensively to explain metal/organic interface dipole formation \[24,25\]. These gap states can be either donor-like (close to the valence band) or acceptor-like (close to the conduction band). A charge neutrality level is then defined as the point separating the donor-like and acceptor-like levels. The charge neutrality level tends to align with the Fermi energy of the electrode as a result of charge transfer between the electrode and the induced gap states, forming an interface dipole. Based on this mechanism GaMnAs with very high hole concentration (~10\(^{20}\)/cm\(^3\)) induces the gap states at GaMnAs/NPB interface. As the charge neutrality level of NPB (4.1 eV – 4.2 eV \[24,25\]) is much smaller than the work function of
GaMnAs (5.27 eV), it is therefore believed that charge transfer occurs between GaMnAs and NPB interface gap states, and an interface dipole is formed, as is shown in figure 3.

5. Conclusion

Interface formation between GaMnAs and NPB is studied by the $J-V$ measurements. The hole injection barrier and vacuum level shift at GaMnAs and NPB interface were estimated to be 0.77 eV and 0.54 eV, respectively, by fitting the measured $J-V$ curves. The band alignment diagram between GaMnAs and NPB is constructed based on the measurement and the calculation. We ascribed the vacuum level shift to charge transfer between GaMnAs and NPB interface gap states. This study should serve as a starting point for the investigation of GaMnAs based organic spin devices.

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