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Improvement of the charge imbalance caused by the use of a p-type silicon anode in an organic light-emitting diode

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Abstract

An indium-tin oxide anode was replaced with a p-type silicon anode in a bilayer small-molecule organic light-emitting diode. As results, the current increased largely due to the enhanced hole injection and the higher conductivity of the Si anode; the luminous efficiency decreased significantly due to carrier-induced exciton quenching and the worse charge imbalance. Ultra-thin film of SiO₂ grown on the silicon anode improved the luminous efficiency to a certain extent by restraining the hole injection; enhancing electron injection became more desired.

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1. Introduction

There have been great efforts over the past decade to obtain technologically viable and efficient light emission from silicon. Among the efforts, silicon quantized systems [1-5], silicon-related direct bandgap materials [6-8], and optically active impurities and defects in silicon [9-12] have been the main emphasis and achieved varying degrees of success. Recently, the organic light emission [13-15] has been applied commercially in full color, flat panel displays. The combination of silicon and organic light-emitting materials will open a route to the integration of optical devices with silicon chips. Organic light-emitting materials are amorphous, rather than crystalline such as GaAs, so there is no lattice mismatch with silicon. They also have the advantages of being relatively easy to make and can emit light of different wavelengths. A few pioneering works of organic

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light emitting diodes (OLEDs) with p-type silicon anodes have been reported [16-19]. However, the performances of the OLEDs with p-Si anodes are relatively low, for example, the highest brightness of the OLEDs with p-Si anodes reported previously was only 100 cd/m^2 at 15 V [16]; more important is that the main reason for the low performance has not been made clear. Zhou et al. [18] anticipated that the OLEDs with p-Si anodes should have higher internal quantum efficiency than those using ITO anodes, but no actual instance has been reported so far. Here, we have fabricated and studied an OLED using a p-Si anode, found that the serious imbalance of the hole and electron injections caused by the p-Si anode should be responsible for the low luminous efficiency, and finally discussed two practical improvement schemes for such devices.

As a surface-emitting OLED, the semitransparent cathode LiF(0.3 nm)/Al(6 nm) with a cap of Au rather than Ag [20] has been chosen in our experiment because Au has a lower reflectance in visible range and a higher chemical stability than Ag. We have not attempted to

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gain a higher transparency by reducing the thickness of Al, and placed emphasis on the essential difference between the p-Si anode and the ITO anode.

2. Experiments

The OLEDs were deposited by vacuum sublimation on to 7–21 Ω cm, p-type (1 0 0) silicon substrates. Prior to the organic deposition these substrates were cleaned using acetone and methanol, followed by the formation of the Al contacts on the backside. First, 60 nm of the hole-transporting layer 4,4-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB) was vacuum (base pressure of 10^{-6} Torr) deposited on the silicon anodes and substrates, followed by 60 nm of the emissive, electron transporting layer: tris-(8-hydroxyquinoline) aluminum) (AlQ) and 0.3 nm of electron injecting layer LiF. 6-nm thick Al cathode followed by a 15 nm cap of Au was then deposited onto the LiF surface through a shadow mask. The resulting device was p-Si/NPB/AlQ/LiF/Al/Au, as illustrated in the inset of Fig. 1a. The two other sets of devices were: p-Si/SiO2/NPB/AlQ/LiF/Al/Au and ITO/ NPB/AlQ/LiF/Al/Au. The SiO₂ layer was grown at 400 °C for 40 min in oxygen atmosphere. ITO-based devices were employed as control samples. All the devices were deposited simultaneously in one chamber without a vacuum break. Electroluminescence (EL) from the diode



Fig. 1. The typical forward I-V (a) and brightness-voltage (b) characteristics for the three sets of devices with different anodes: ITO, p-Si and p-Si/SiO2. Inset: some characteristic voltages in the brightness-voltage curves.

was collected in air by a fluorescent spectrometer (SPEX FL-11), and the brightness was calibrated by a PR650 spectrometer. Current–voltage (*I–V*) measurements were made by $6^{1}/_{2}$ -digit multimeters (HP 34401). The ultraviolet photoemission spectroscopy (UPS) spectra were performed on a multi-technique electron spectrometer (VG ESCA-LAB MKII) with the He I radiation (*hv* = 21.2 eV) under a base pressure of 1.0×10^{-8} Pa.

3. Results

Fig. 1 shows the typical forward I-V and brightnessvoltage characteristics for the three sets of devices with different anodes: ITO/NPB/AlQ/LiF/Al/Au, p-Si/NPB/ AlQ/LiF/Al/Au, and p-Si/SiO₂/NPB/AlQ/LiF/Al/Au. As can be seen from Fig. 1a, the current for the device with the p-Si anode rises much faster with voltage increasing, and is much higher than that for the device with the ITO anode. For example, the former is 21 mA at 10 V, higher than the latter by a factor of ~ 10 . Another difference is that the I-V curve for the device with the ITO anode shows distinct two regimes [21]. The current increased evidently faster above 9 V, which is not seen for the device with the p-Si anode. For the device with the p-Si /SiO₂ anode the current has been decreased evidently, for example, by about 50% at 10 V in relation to the device current with the p-Si anode. In Fig. 1b, the brightness of the device with the ITO anode is measured from the top cathodes, the transparency of which is 20%. As whole, the brightness for the device with the p-Si anode is lower. The insertion of SiO_2 has enhanced the brightness evidently, but is still lower than the brightness of the device with the ITO anode. Some characteristic voltages are showed in Fig. 1b as an inset. The turn-on voltage is defined as the applied voltage at a luminance of 1 cd/m^2 . With the ITO anode, the maximum luminous efficiency η is calculated to be 0.34 lm/ W at 7 V; with the SiO₂/p-Si anode, the maximum luminous efficiency is 0.017 lm/W, higher than that with the p-Si anode by ~ 5 times.

For estimation of the electron contribution to the total current in the above devices, other three sets of 'hole only' devices ([22] this is the case at least at low voltages before emitting light) with 15-nm-thick Au cathodes have been made: ITO/NPB/AlQ/Au, p-Si/NPB/AlQ/Au, and p-Si/SiO₂/NPB/AlQ/Au. Their I-V curves are shown in Fig. 2 to compare with their counterparts with LiF/Al/Au cathodes. The current for the device with the Au cathode is slightly lower in the low-voltage regime, but evidently lower in high-voltage regime than that for its counterpart with the LiF/Al/Au cathode. The hole current dominates the current of the bipolar devices and the contribution of the electron current is small.



Fig. 2. Comparison of the I-V characteristics for the devices with the same anode (p-Si, p-Si/SiO₂ or ITO) but different cathodes: LiF/Al/Au, and Au.

Fig. 3 shows the He I UPS spectra of the p-Si substrate and the 1- and 15-nm NPB on the p-Si substrate. The UPS spectrum of p-Si was collected after the in situ removal of NPB by Ar ions beam. To ensure the collection of low-energy electrons, samples were biased at negative 4 V. The ionization potentials of organic materials



Fig. 3. (a) HeI UPS spectra of the p-Si, the 1- and 15-nm NPB on p-Si; The determination of the thresholds at highest kinetic energy in the UPS spectra of Si (b) and NPB (c).

and p-Si can be readily determined by subtracting the width of the UPS spectrum from the energy of the He I radiation. The UPS spectrum width is the energy difference between the intensity thresholds at the highest and lowest kinetic energy. The thresholds at highest kinetic energy in the UPS spectra of Si and NPB are determined to be 20.40 and 19.9 eV as indicated in Figs. 3b and c, respectively; the thresholds at the lowest kinetic energy, i.e. cutoffs are easy to identify, which are 4.25 and 3.90 eV, respectively. In this way, the ionization potential of NPB and the p-Si were determined to be 5.20 and 5.05 eV. The former is in good agreement with that reported in [23]. Considering the energy bending at the p-Si surface and the Fermi level of p-Si, the latter is consistent with that reported in [24] and [18]. As indicated in Fig. 3, there is an offset of 0.35 eV between the cutoffs in their UPS spectra, which is demonstrated due to the charging effect of the NPB layer rather than due to the interfacial dipoles. The characteristic emission of C^{1s} in 15-nm NPB was calibrated by X-ray photoemission spectroscopy, which gave an identical shift of the kinetic energy offset to lower values as in the UPS spectra due to charging effects, moreover, the shift of the kinetic energy offset to lower values upon increasing the NPB thickness can be due to charging effects.

Fig. 4 depicts the alignment of their energy levels. A potential barrier of about 0.15 eV between NPB and p-Si is determined. This value is considerably smaller than that at the ITO/NPB interface reported in [23] (1.4 eV, including 0.5 eV interface dipole shift) and [25] (0.5 eV). The work function of ITO is 4.70 eV measured in our experiment, consist with the commonly reported values from $4.4 \sim 4.7$ eV for the ex situ treated ITO [25–27], so the hole barrier at the ITO/NPB interface is also deduced to be about 0.50 eV if neglecting the existence of the dipoles at this interface.



Fig. 4. The energy level alignment for the p-Si and NPB.



Fig. 5. Luminous efficiency-voltage curves for the devices with different anodes (p-Si or ITO) and different cathodes (with LiF or with no LiF).

In Fig. 5, the impacts of LiF (0.3 nm) on the luminous efficiency [28] for two sets of devices with different anodes (p-Si and ITO) are compared: p-Si/NPB/AlQ/ LiF/Al/Au and p-Si/NPB/AlQ/Al/Au; ITO/NPB/AlQ/ LiF/Al/Au and ITO/NPB/AlQ/Al/Au. For the device with the p-Si anode, the insertion of LiF enhances the efficiency by ~ 10 times, but for the device with the ITO anode, only by 3 times.

4. Discussions

The use of p-Si as anode has lead to a higher current at a lower driving voltage; the hole injection barrier between p-Si and NPB is as little as ~0.15 V demonstrated by UPS. Judged only by these facts, p-Si is an ideal choice for hole injection. But, the enhanced hole injection (due to the lower hole barrier) results in a worse electron-hole imbalance. The OLEDs of ITO/NPB/ AlQ/LiF/Al/Au and p-Si/NPB/AlQ/LiF/Al/Au are completely identical except for the anodes; the electron injection is equal, thus the enhanced current should be contributed to enhanced holes. The fact that the I-Vcurves for the OLEDs with LiF/Al/Au cathodes are close to those for the 'hole only' devices at low voltages also suggests this viewpoint. Moreover, the higher conductivity of the p-type Si anode will enhance the hole charge density injected to NPB resulting in increased hole-leakage current. Thus, the increased current has not resulted in an increased luminance as expected [18]. Both the turn-on voltage and the operating voltage for a luminance of 100 cd/m^2 increase significantly when an ITO anode is replaced with a p-Si anode. This is believed due to the worse hole-electron imbalance. At low voltages, a larger proportion of the total current is holeleakage current in the OLED with a p-Si anode compared with that with an ITO anode where holes are already the majority carriers, so fewer injected electrons can form excitons with holes to recombine to emit light; as the voltage increases, the contribution of the injected electrons to the recombination current increases, then the device begins emitting light efficiently. The luminance decrease may be due to carrier-induced exciton quenching as a significant increase of the hole concentration is expected in AlQ near the NPB/AlQ interface as a result of the enhanced hole injection that takes place at significantly lower voltages. Another contributing factor may be the reduced electron-hole balance (also as a result of the increased hole density) that reduces the recombination efficiency and thus the exciton formation probability in these hole-dominated OLEDs.

To improve the charge imbalance caused by the use of a p-Si anode, decreasing the hole current is necessary, so the thin SiO_2 film has been grown on the p-Si anode. The thin SiO_2 film can also passivate the silicon surface and reduce the surface recombination current. It is believed optimistically that deliberate use of thin SiO_2 layer or other hole-blocking layers can enhance the EL efficiency further [29].

On the other hand, electron injection should be enhanced. In the conventional small-molecule OLEDs, electron is minor-injected carrier, and determines the EL efficiency. In the OLEDs with the p-Si anode, the enhancement of electron injection becomes more desired. As indicated in Fig. 5, for the device with the p-Si anode, the insertion of LiF enhances the efficiency by a greater factor in relation to that for the device with the ITO anode. This fact clearly indicates that electrons are the minority carriers in the OLED with a p-Si anode, and more important point here is that it suggests the charge imbalance in these devices is significantly worse than in the OLEDs with an ITO anode. Selection of the topics in our future study.

5. Conclusion

Using p-Si as anode in OLEDs enhances the hole injection largely, but leads to an significant decrease in luminous efficiency. Ultraviolet photoemission spectroscopy study shows a potential barrier of 0.15 eV between the p-Si anode and hole transporting layer, NPB. The relatively low efficiency should be attributed to carrier-induced exciton quenching and the serious charge imbalance. Ultra thin SiO₂ film grown on the silicon can act as hole-blocking layer, and improve the luminous efficiency markedly.

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