Thin Solid Films 518 (2009) 791–794

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Internal photoemission spectroscopy measurement of Alq_3/cathode interface by three layered electron only device

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ARTICLE INFO

Available online 29 July 2009

Keywords:
Internal photoemission
Barrier height
Alq_3
Electron only device

ABSTRACT

We have investigated the Schottky barrier height for electrons at aluminum tris (8-hydroxyquinoline) (Alq_3)/cathode interfaces by internal photoemission (IPE) measurement. A three layered device consisting of ITO/TiO_2/intermediate layer (IL)/Alq_3/cathode structure was used to fabricate the "electron-only device" and to reduce the equivalent thickness of TiO_2 and IL stack. The measured barrier heights were 0.86, 1.05, 1.3 and 1.55 eV for MgAg, Al, Ag and Au electrodes, and it gradually decreased with external voltage and it was explained as Schottky effect. Barrier height showed linear relationship with work-function and electronegativity of cathode materials. The slope parameter of 0.6 with electronegativity was attributed to the interfacial charge transfer through the metal-induced gap states at the cathode/Alq_3 interface.

1. Introduction

The interface properties of metal/insulator and metal/semiconductor attract an unprecedented attention especially in the field of metal oxide insulators with high dielectric constant (high-*k*) in advanced metal–oxide-insulator (MOS) devices [1,2], and organic semiconductor devices [3–8]. Organic devices such as organic light emitting diode (OLED) and organic field effect transistors (OFET) are attracting a great deal of attention recently and device operations of OLED and OFET requires the charge injection from electrode material into the organic semiconductor layer. Therefore, the estimation of barrier height for the charge injection of electrons and holes at the electrode/organic interface is essentially important. In general, the barrier height for electrons is assumed as the difference of the lowest unoccupied molecular orbital (LUMO) of organic material, and the work functions of the cathode. However, the reported value of work functions has a strong variation depending on the measuring method and the surface states, and the interfacial dipole moment also modify the barrier height seriously [3–9]. The direct measurement method for the barrier height at the electrode/organic interface is required under the device operation. Internal photoemission (IPE) spectroscopy provides the most straightforward way to characterize the relative energies of electron states at interfaces of insulators (or wide-gap semiconductor) from the Fermi level of metals by measuring the spectral onset of electron/hole photoemission from one solid into another [1,2,6–8]. However, in general, it is difficult for organic devices to reduce the leakage current less than 1 nA/cm^2 under the electric field with the order of 10^5 V/cm except for OFET with robust gate insulator, while the typical measured IPE current is only the order of 0.1–10 nA/cm^2 under this high electric field and the illumination of monochromatic light of 1 mW/cm^2. Moreover, IPE of electrons are emitted from the cathode while IPE of holes is possible from the anode. Thus, currently, IPE technique is not popular in organic thin film devices and the external photoemission spectroscopy technique has been popular and revealed the interface phenomena in electrode/organic materials [3–5]. One may consider that IPE technique is, nevertheless, useful technique for understanding the interface phenomena especially under electric field when it is possible to suppress the leakage current and IPE of holes from the counter electrode sufficiently.

In this study, we have fabricated the three layered structure consisting of TiO_2 layer deposited on indium tin oxide (ITO), very thin intermediate layer, and aluminum tris (8-hydroxyquinoline) (Alq_3) layer which is covered by various types of cathode. IPE of holes and the leakage current in this device can be suppressed due to the hole blocking property of underlying TiO_2 and intermediate layer (IL). Moreover, most of the external voltage is applied to Alq_3 layer and electrons can transport easily through TiO_2 and IL because TiO_2 is high-*k* ($\varepsilon_r > 40$) electron transporting material and IL is very thin electron transporting film. That is, this device structure is considered as very nice "electron only device" suitable for IPE measurement even various cathode materials with different work-function are used.

2. Experimental

Precursor solution for anatase phase TiO_2 consisting of 0.5 mol/l of titanium tetraisopropoxide (TTI), diethanolamine (DEA), and water dissolved in ethanol was spin-coated onto 20 nm-thick indium–tin-oxide (ITO) coated glass substrate followed by heat-treatment at a temperature of 450 °C [10,11]. The width of ITO pattern was 2 mm and the thickness of anatase TiO_2 layer was about 100 nm. IL and

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doi:10.1016/j.tsf.2009.07.087

Alq_3 layers were then deposited by vacuum sublimation onto the TiO_2 layers. We chose 30 nm (or 20 nm)-thick-5, 10, 15, 20-tetra (4-pyridyl) porphyrin (H_2TPyP) or 30 nm-thick-bathocuproine (BCP) as IL. The thickness of Alq_3 was 150 nm. The base pressure used was about 3×10^{-6} Torr and deposition rate for H_2TPyP, BCP and Alq_3 were 0.1 nm/s, 0.1 nm/s and 0.3–0.4 nm/s. Finally, 50 nm-thick Au, Ag, Al and MgAg (10:1) were thermally evaporated as cathode. The electrode area was $0.2 \times 0.2\ cm^2$. Here, the equivalent thickness of TiO_2/IL stack to Alq_3 as a dielectric was about 30 nm, and most of the external voltage was then applied to Alq_3 layer.

Charge carriers overcoming the interface barrier were measured from photocurrent generated by the drift of the electrons from cathode to ITO electode in a temperature controlled vacuum chamber. The IPE current was determined as the difference between the photocurrent measured under illuminating the sample through ITO electrode and the one measured in darkness, using a electrometer (Keithley 617). The monochromatic light was illuminated through monochlomator (SHIMADZU SPG-120) and optical low-pass filter by halogen lamp and optical low-pass filter from 1550 nm to 900 nm or from 1100 nm to 600 nm. Here, full width at half maximum (FWHM) of the wavelength of incident light through monochromator was less than 5 nm, and the resolution of photon energy was therefore less than 0.01 eV.

3. Results and discussions

Fig. 1 shows the energy diagram and chemical structure of materials used in this study. The work-functions of Au and ITO electrodes were estimated to be 4.75 eV and 4.8 eV from low energy photo-electron emission measurement under ambient atmosphere by AC-2 (Riken Keiki Co. Ltd.). The work function of MgAg, Al, and Ag was measured from the contact potential difference between Au electrode and these metal electrodes [10–12]. The work-function of Al, MgAg, Ag electrodes were then estimated as 4.0, 3.7, 4.3 eV. The values of ionization potential (or the highest occupied molecular orbital: HOMO) of organic material were also obtained by AC-2, and the values of the lowest unoccupied molecular orbital (LUMO) which were estimated by subtracting the optical band gap from HOMO values. As can be clearly seen in Fig. 1, the energy diagram at the TiO_2 and each dye interface favors a smooth transfer of electrons from Alq_3 into H_2TPyP (IL) as well as the transfer of electrons from IL into TiO_2.

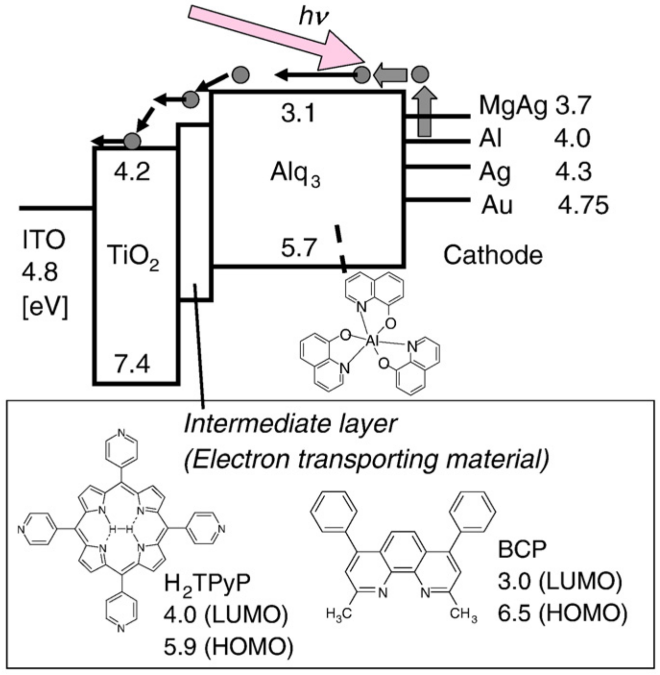

Fig. 1. The energy diagram and chemical structure of materials used in this study.

Fig. 2(a) shows the typical IPE spectra of electrons photo-injected from MgAg into Alq_3. Here, IPE yield in Fig. 2(a) is calculated as the incident photon to current-conversion efficiency (IPCE),

$$IPCE = \frac{1240 \times \mathit{photocurrent\ density}[\mathrm{mA / cm^2}]}{\mathit{wavelength}[\mathrm{nm}] \times \mathit{total\ incident\ photon\ flux}[\mathrm{mW / cm^2}]}. \quad (1)$$

For wavelength $\lambda > 1450$ nm (0.85 eV) only the noise signal or very small leakage current in the order of 0.1–10 pA (dependent on external voltage) could be detected. IPCE signal increased continuously with the increase of photon energy (or decrease of wavelength) for wavelength $\lambda < 1450$ nm. Here, the typical incident photon flux was in the order of 1 mW/cm^2 and then the photocurrent density at 1240 nm was about 0.1 nA/cm^2 (4 pA) when IPCE value gave 10^{-5}%. According to Fowler theory, the photocurrent quantum yield Y_{IPE} for electrons excited from states close to the Fermi level of a metal into semiconductor conduction band is given as [13]

$$Y_{IPE} \propto (h\nu - \phi_e)^2, \quad (2)$$

if $h\nu > \phi_e$, where $h\nu$ is photon energy, ϕ_e the barrier height for electrons at certain voltage. Fig. 2(b) shows the $(IPCE)^{1/2}$–$h\nu$ curves of the result in Fig. 2(a), and better linearity in Fig. 2(b) is likely to

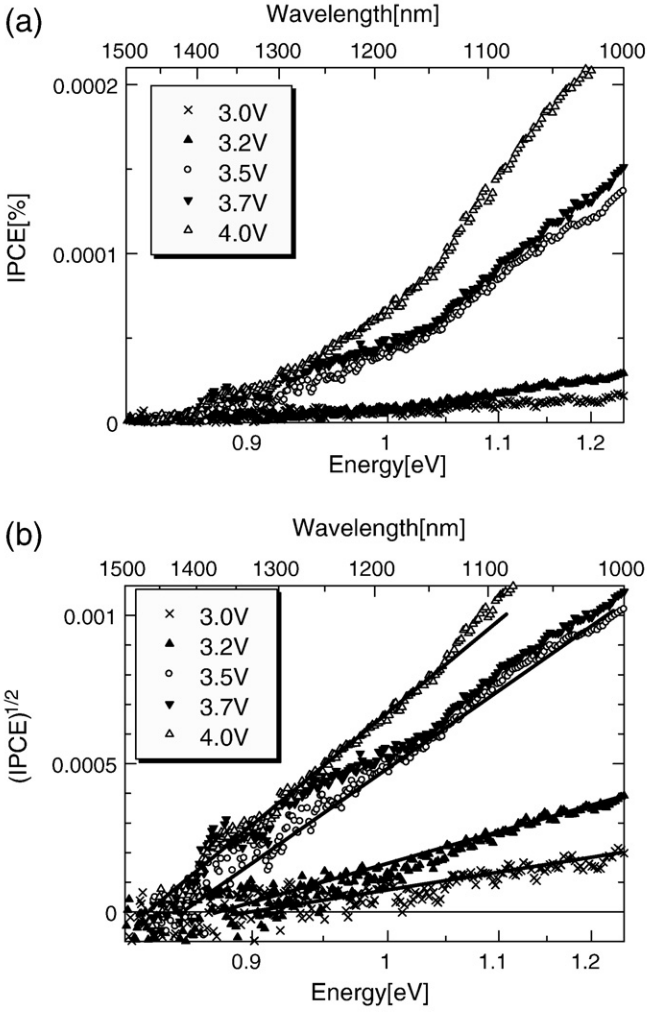

Fig. 2. (a) The typical IPE spectra of electrons for ITO/TiO_2 (100 nm)/H_2TPyP (30 nm)/Alq_3 (150 nm)/MgAg measured at various external voltage, (b) $(IPCE)^{1/2}$–$h\nu$ plots for the data in Fig. 2(a).