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Measurement of ultralow injection current to polymethyl-methacrylate film

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Ultralow electron/hole injection currents from an electrode to a polymethyl-methacrylate (PMMA) film can be accurately decided by measuring the slow shift in the flatband voltage of a metal-insulator-semiconductor (MIS) device. It has been found that both the electron and hole injection currents are limited by the metal/PMMA interface and can be roughly described with a modified Richardson–Schottky equation. The space charge or dipole relaxation in PMMA films has been observed as well, which induces an instant change in flatband voltage of the MIS devices. These properties are critical issues for the stability of organic thin film transistors with PMMA gate insulator. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2948853]

Organic electronic devices have gained considerable interest due to their broad potential applications and various advantages over inorganic counterparts, including low cost, light weight, flexibility, and easy fabrication.[1] Although most of the studies are focusing on organic semiconductor materials, organic insulators have been found to be equally important for the performance of organic devices, especially for organic thin film transistors (OTFTs).[2] The properties of the gate insulator in a TFT, including the dielectric properties and the leakage current, play an important role on the device performance and the stability.[3,4] In addition, it has been reported that the performance of some photosensitive OTFTs is based on the mechanism of carrier injection at the semiconductor/insulator interface.[5] It is worth noting that even ultralow injection current in the gate insulator may induce a pronounced shift of flatband voltage after long enough time since the flatband voltage is influenced by the accumulation of injected charge. Therefore study on charge injection to organic insulators will help understand the performance of OTFTs.

The leakage current of an insulator material can be directly measured on a capacitor structure with two metal electrodes on both sides of the insulator film. However, sometimes the leakage current that can be measured is the current across some short paths due to impurities or nonuniform locations in the film. On the other hand, the electron/hole currents cannot be separately obtained. Therefore, we have developed a technique for characterizing ultrasmall electron/hole current in an insulator. In this study, we have chosen polymethyl-methacrylate (PMMA), which is one important polymer insulator that has been widely used in OTFTs as gate insulator[6,7] and organic light emission diodes as charge blocking layer.[8]

As shown in Fig. 1, a metal-insulator-semiconductor (MIS) device is used in the measurement. The MIS capacitor is fabricated on a lightly doped *n*-type silicon wafer with a thin thermal oxide layer. SiO_2 thickness is 50 nm. Resistivity of the Si is about $1-5\ \Omega\,cm^{-1}$. Doping level is about $3.3\times10^{15}\ cm^{-3}$. PMMA ordered from Sigma-Aldrich is dissolved in methyl ethyl ketone (MEK) solution and spin coated on the SiO_2 film. The thickness of PMMA layer is 560 nm. Then a top electrode with an area of 1 mm^2 is deposited on the PMMA film. To study the influence of electrodes on the leakage current, we have used both inorganic and organic electrodes, i.e., Au and poly(3,4-ethylenedioxythiophene)/poly(styrene-sulfonic acid) (PEDOT/PSS). A layer of Al is evaporated on the back of Si wafer to get a better contact on the other side.

The capacitance-voltage (*C-V*) curves are measured with the system described previously.[9] Bias voltage at the top electrode can cause the transport of mobile ions inside the insulator, being reflected on the parallel shift of *C-V* curve. With the progressive bias voltage, the ion transport as a function of time can be obtained. In this analysis, the ion transport can be characterized by the parallel shift of *C-V* curve. However, error can be introduced by measuring the curve shift after the stressing cycle, as the sweeping voltage for the *C-V* curve is different from the bias voltage and therefore will upset the charge distribution. To reduce the error, we measure one *C-V* curve before a bias stress. During the stressing cycle, we do not measure the whole *C-V* curve to obtain the parallel shift, instead only a capacitance at a certain fixed voltage V_m (normally $V_m=0$) is measured at intervals and the change in capacitance will reflect the change in flatband voltage of the device. Therefore the measuring time can be reduced to the least in order to minimize the error

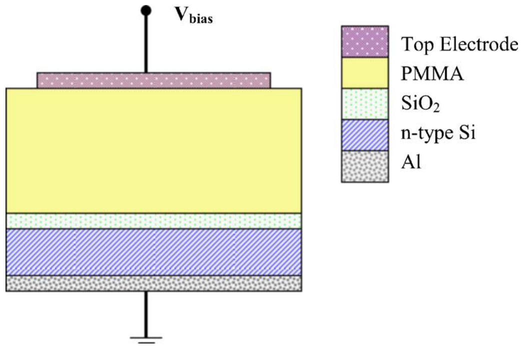

FIG. 1. (Color online) Cross-sectional view of the MIS device used for characterizing the charge injection in a PMMA film.

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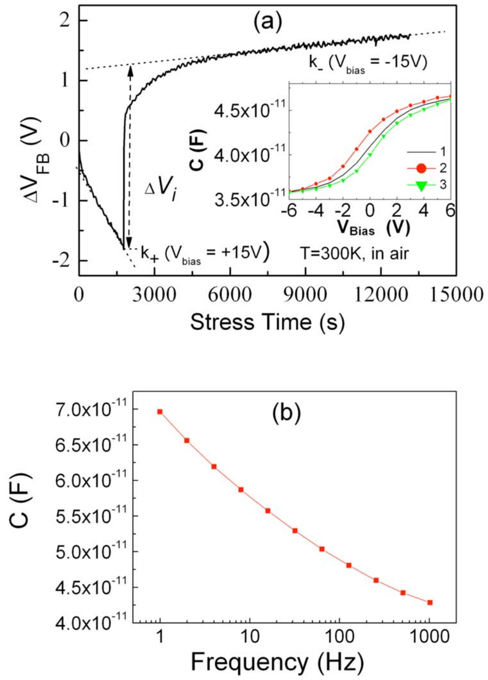

FIG. 2. (Color online) (a) Shift in flatband voltage of a Au/PMMA/SiO$_2$/N-Si MIS device under ±15 V bias voltage measured in air. The dash lines correspond to the least square fitting of the experimental results in linear regions. Inset: *C*-*V* curves of the MIS device measured at the frequency of 100 Hz. Curve 1: fresh sample; curve 2: after being biased at +8 V for 100 min; curve 3: after being biased at −8 V for 400 min. (b) Frequency dependent capacitance of the MIS device under positive bias voltage of 20 V.

from the capacitance measurement. Assuming under bias stressing V_{bias} the *C*-*V* curves have parallel shift only, which is the case in the experiment, the flatband voltage shift of the MIS device can be calculated from the capacitance change, which will be automatically done with a computer. The capacitance is measured at the frequency of 100 and 10 Hz for devices with Au and PEDOT/PSS electrodes, respectively, since the conductivity of PEDOT/PSS is found to be not big enough for higher frequency measurement. The devices are measured in both vacuum and air to find the ambient influence on the charge injection process.

C-*V* curves of an Au/PMMA/SiO$_2$/Si device measured in air are shown in the inset of Fig. 2(a). After being biased at positive/negative 8 V for a certain period of time, the *C*-*V* curve shifts horizontally to negative/positive voltage, respectively. Figure 2(a) shows the flatband voltage shift ΔV_{FB} of the *C*-*V* curve of the device under bias stressing in air, which is calculated from the capacitance change. Both positive and negative bias stressing effects have been measured. Since the control device with Au/SiO$_2$/Si structure shows no shift of *C*-*V* curve under bias stressing, the shift that we have observed can be attributed to space charge diffusion in the PMMA layer. The voltage shift can be divided into two domains: instant change in a short time domain ΔV_i and slow change in a long time domain, which are due to different mechanisms. The flatband voltage of a MIS device is related to the distribution of space charge in the insulator layer, as given in Eq. (1)

$$V_{\mathrm{FB}} = -\frac{1}{\varepsilon_r \varepsilon_0}\{Q_+ c_+ + Q_- c_-\} + \Delta\psi_f, \tag{1}$$

where, ε_r is the relative dielectric constant of the insulator. Q_+ and Q_- are the positive and negative charge density per unit area in the insulator film, c_+ and c_- are the distances of the centroids of positive and negative charges from the metal/insulator interface, and $\Delta\psi_f$ is the potential difference between the Fermi level of the Si and the top gate. Here, the effect of interface charge between Si and SiO$_2$ is neglected.

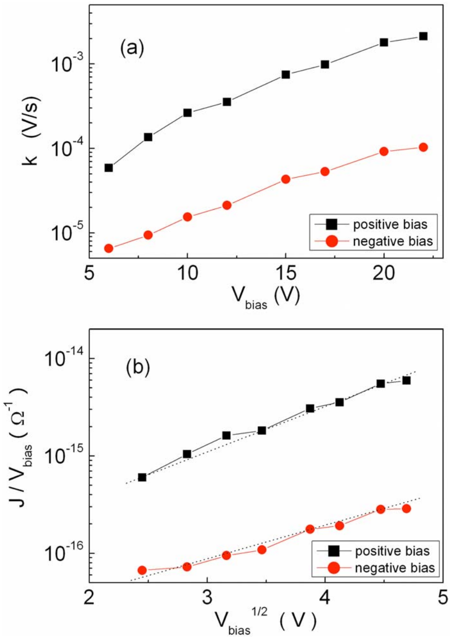

FIG. 3. (Color online) (a) Changing rate ($k_\pm$) of the flatband voltage of an Au/PMMA/SiO$_2$/*n*-Si device under different positive and negative bias voltages. (b) Injection current of electron/hole under different bias voltages.

The instant change in flatband voltage ΔV_i is approximately proportional to the bias voltage. We assume that the instant change can be attributed to the relaxation of space charge or dipoles in the PMMA film. To confirm this assumption, the capacitance of the MIS device under a bias voltage of +20 V has been measured at different frequencies in vacuum, as shown in Fig. 2(b). The capacitance exhibits big frequency dispersion, which is normally attributed to pronounced space charge or dipole relaxation in the PMMA film.[10]

In the long time domain, both positive and negative bias voltages can induce linear changes in flatband voltage with bias time. Figure 3(a) shows the changing rate *k* as a function of bias voltage. Here, SiO$_2$ layer shows much better insulating property than PMMA layer.[11] Therefore the slow change in flatband voltage of the device can be attributed to charge injection from the top electrode to the PMMA layer. The positive and negative voltage shifts correspond to electron and hole injection, respectively. Since the injection charge is blocked by the SiO$_2$ layer, the total moving distance of the charge is approximately the thickness of PMMA layer. The changing rate of flatband voltage related to injection current is derived from Eq. (1),

$$\frac{dV_{\mathrm{fb}}}{dt} = \begin{cases} -\dfrac{1}{\varepsilon_r\varepsilon_0}\dfrac{dQ_+}{dt}\delta = -\dfrac{\delta}{\varepsilon_r\varepsilon_0}I_h & V_{\mathrm{bias}} > 0 \\ -\dfrac{1}{\varepsilon_r\varepsilon_0}\dfrac{dQ_-}{dt}\delta = \dfrac{\delta}{\varepsilon_r\varepsilon_0}I_e & V_{\mathrm{bias}} < 0, \end{cases} \tag{2}$$

where δ is the thickness of the PMMA layer, I_h and I_e are hole and electron injection currents, respectively. Therefore

TABLE I. List of testing conditions, fitting parameters, and injection currents of different MIS devices.

Electrode	Au	Au	Au	PEDOT:PSS	PEDOT:PSS
Ambient	Air	Air	Vacuum	Air	Vacuum
Injection carriers	Electron	Hole	Hole	Hole	Hole
β($\mathrm{V}^{-1/2}\ \mathrm{m}^{1/2}$)	6.2×10^{-4}	8.2×10^{-4}	8.0×10^{-4}	9.7×10^{-4}	7.2×10^{-4}
Injection current at $\lvert V_{\mathrm{bias}}\rvert=15$ V	5.7×10^{-15}	1.1×10^{-13}	1.0×10^{-13}	3.4×10^{-15}	3.8×10^{-15}

this method can be used to measure ultralow electron/hole injection current independently.

As shown in Fig. 3(b), the relationship between injection current and bias voltage is obtained, which can be fit pretty well with the thermionic emission process since $\ln(J/V_{\mathrm{bias}})$ shows a linear relationship with $\sqrt{V_{\mathrm{bias}}}$. The mobility of charge in PMMA film is very low; thus we consider that a modified Richardson–Schottky equation proposed by Simmons[12] can be used to describe the leakage current as given below,

$$J=\alpha T^{3/2}E_0\mu\left(\frac{m^*}{m}\right)^{3/2}\exp(-\phi_b/kT)\exp(\beta\sqrt{E_0})$$

$$\beta=(e/kT)(e/4\pi\varepsilon_r\varepsilon_0)^{1/2}, \tag{3}$$

$\beta=(e/kT)(e/4\pi\varepsilon_r\varepsilon_0)^{1/2}$, where, $\alpha=3\times10^{-4}$ A s/cm^3 K$^{3/2}$, μ is the carrier mobility in the insulator, E_o is the electric field across the barrier, m^* and m_0 are the mass of carriers and free-electron mass, respectively, ϕ_b is the potential barrier height, and ε_r is the relative dielectric constant of PMMA. In this model, there is no clear distinction between bulk and electrode limited conduction mechanisms as shown in Eq. (3) because each plays a part in the conduction process. Since the dielectric constant of PMMA and SiO$_2$ is very similar,[7] the electric field can be approximately given by $E_0=V_{\mathrm{bias}}/(\delta+\delta_{\mathrm{ox}})$, where δ and δ_{ox} are thickness of PMMA and SiO$_2$ layer, respectively. Therefore the slope of $\ln(J/V_{\mathrm{bias}})$ versus $\sqrt{V_{\mathrm{bias}}}$ is $\beta/\sqrt{\delta+\delta_{\mathrm{ox}}}$ and the value of β can be obtained to compare with the value given in Eq. (3). Given the dielectric constant of PMMA (Ref. 13) $\varepsilon_r=3.5$, we can get $\beta=7.8\times10^{-4}$ V$^{-1/2}$ m$^{1/2}$. For comparison, the value of β for both hole and electron injection is extracted from the injection current, as shown in Fig. 3(b). The dash lines correspond to the least square fitting of the experimental results. As shown in Table I, β of hole injection current is very close to the theoretical value while that of electron injection is a little bit lower. This result indicates that the modified Richardson–Schottky model can be used to explain the injection current to PMMA layer. The same sample is characterized in vacuum and shows little difference on the injection current, as shown in Table I, indicating that PMMA film is rather stable in air.

Although the injection current to PMMA film can be roughly fitted with the modified Richardson–Schottky equation, it is difficult to imagine the existence of a valence/conduction band in a PMMA film. We assume that there is a dominant conduction level in PMMA, which is due to a distribution of localized states. As reported by Baranovskii *et al.*,[14] charge transport due to variable range hopping process in a continuously distributed trap states with a function of $g(\in)\propto\exp[-(\in/\in_0)^{\lambda}]$ ($\lambda=2$ for polymers) shows a transport energy level in the system. Therefore it is reasonable to use the modified Richardson–Schottky equation to describe the injection current to PMMA film. The deviation of β from the theoretical value may be attributed to the broad distribution of states in the PMMA film, which is different from normal semiconductor materials.

For the device with a PEDOT/PSS electrode, we just study the hole injection current since the electron injection current is so small that it takes too long time for one measurement. To study the ambient influence on charge injection behavior, the devices have been characterized both in air and vacuum, as shown in Table I. It is interesting to note that the device with a PEDOT/PSS electrode shows different leakage currents in air and vacuum, which is probably due to the absorption of H$_2$O in the PEDOT/PSS electrode when it is measured in air.

We suggest that any organic insulator used in OTFT can be characterized by this technique. The influence of gate insulator on the performance of OTFT can be divided into two parts. One is the space charge or dipole relaxation in the insulator film which can induce an instantaneous change in the flatband/threshold voltage. This effect can be regarded as the result of an increase in the gate capacitance. Another part is the charge injection from both sides of the gate insulator. The induced slow shift in flatband voltage is dependent on the distribution of injected electron/hole charge in the gate insulator, as given in Eq. (1).

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