High-mobility, low-power, and fast-switching organic field-effect transistors with ionic liquids

S. Ono, S. Seki, R. Hirahara, Y. Tominari, and J. Takeya

Related Articles

Strain control of AlGaN/GaN high electron mobility transistor structures on silicon (111) by plasma assisted molecular beam epitaxy
J. Appl. Phys. 111, 114516 (2012)

HfO2 dielectrics engineering using low power SF6 plasma on InP and In0.53Ga0.47As metal-oxide-semiconductor field-effect-transistors
Appl. Phys. Lett. 100, 243508 (2012)

Electrical instability of amorphous indium-gallium-zinc oxide thin film transistors under monochromatic light illumination
Appl. Phys. Lett. 100, 243505 (2012)

Dual-purpose BGaN layers on performance of nitride-based high electron mobility transistors
Appl. Phys. Lett. 100, 243503 (2012)

Simulation of tunneling field-effect transistors with extended source structures
J. Appl. Phys. 111, 114514 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

High-mobility, low-power, and fast-switching organic field-effect transistors with ionic liquids

S. Ono,[1,a)] S. Seki,[1] R. Hirahara,[2] Y. Tominari,[2] and J. Takeya[2,3]

[1]*Central Research Institute of Electric Power Industry, Komae, Tokyo 201-8511, Japan*
[2]*Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan*
[3]*PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*

We report high-mobility rubrene single-crystal field-effect transistors with ionic-liquid (IL) electrolytes used for gate dielectric layers. As the result of fast ionic diffusion to form electric double layers, their capacitances remain more than 1 μF/cm^2 even at 0.1 MHz. With high carrier mobility of 1.2 cm^2/V s in the rubrene crystal, pronounced current amplification is achieved at the gate voltage of only 0.2 V, which is two orders of magnitude smaller than that necessary for organic thin-film transistors with dielectric gate insulators. The results demonstrate that the IL/organic semiconductor interfaces are suited to realize low-power and fast-switching field-effect transistors without sacrificing carrier mobility in forming the solid/liquid interfaces. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2898203]

Field-effect transistors (FETs) based on organic semiconductors have been extensively investigated for the recent decade, in which realizing high-mobility, low-power, and fast-switching devices has been a central subject to take the best advantage of their simple and low-cost production processes.[1] For this purpose, the material combination in the layered structure of organic FETs is being intensively studied because the interfacial phenomena are crucial in determining their device performances. While most of the studies for device applications are based on thin-film organic polycrystalline semiconductors, organic single-crystal FETs are advantageous to study because of its intrinsic material potentials and the interfacial properties both at the semiconductor-electrode and the semiconductor-insulator boundaries in the absence of the grain boundaries.[2–4] Recently marked progresses in the studies of the single-crystal transistors have been achievements of mobility exceeding 20 cm^2/V s (Refs. 5–8) which is already much higher than that of amorphous silicon transistors, and detection of the normal Hall effect, evidencing the bandlike transport mechanism.[9,10]

Most common gate dielectrics used for the organic FETs are typically 100–500 nm thick SiO$_2$ or polymer layers, whose capacitances are in the range of 5–30 nF/cm^2. With such relatively low capacitance, the maximum carrier density is limited in the order of 10^{13} cm^{-1} even at the gate voltage V_G of 100 V, which is already close to dielectric breakdown.[11] As one of the alternative methods to accumulate carriers more efficiently, there have been significant interest in making use of electrolytes. When V_G is applied to the electrolytes, electric double layers (EDLs) are formed after the ionic redistribution, so that V_G is sustained only at typically 1 nm thick EDLs. As the result, capacitance of the EDLs exceeds ~10 μF/cm^2, meaning that orders of magnitude higher density carriers are accumulated at the surface of the semiconductors at the same V_G as compared to those in the SiO$_2$ organic FETs. Recently, it has been demonstrated by several groups that the devices with polymer electrolytes are indeed successful for the high density carrier

accumulation.[12–19] A drawback of the polymer electrolytes, however, is their slow ionic diffusion before the EDL formation, which is actually fatal to the switching speed of the transistors. Moreover, many devices with the polymer electrolytes suffer from serious deterioration in carrier mobility due to possible damages at the interface to the organic semiconductors, which reduces the merit of the EDL-FETs.

In this letter, we introduce ionic liquids (ILs), also known as room-temperature molten salts, for the electrolyte in the rubrene single-crystal EDL-FETs. Without any solvent, ILs show distinctive properties of high thermal stability and no volatility, therefore attracting interests in the material properties themselves.[20] The advantage of the ILs electrolyte in the OFETs is its high-speed formation of the EDLs; the rapid ionic diffusion of the ions typically in ~1 μs is translated into 1-MHz-switching OFETs. We also show that it is possible to keep the surface of the rubrene crystal relatively in a good condition by choosing a proper compound for the ILs, so that mobility of 1.2 cm^2/V s is realized. As the result, sufficiently large on current is achieved even with the gate voltage less than 0.5 V, with the benefit of the large capacitance of the EDLs.

The ILs which we use in this experiment are 1-ethyl-3methylimidazolium bis(fluorosulfonyl)imide (EMIFSI) and 1-ethyl-3methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI); the structure of these materials are shown in Fig. 1(a). These ILs in the imidazolium family have been known to have rather high ion conductivity at room temperature [($\sim$2–3)$\times$10^{-2} S/cm] and widely used in the studies for potential application in a variety of solid state electrochemical devices, such as fuel cells,[21] and lithium batteries.[22,23]

We have placed a droplet of IL electrolyte under a gold wire for a gate electrode on top of a rubrene single crystal to form the Au/IL electrolyte/rubrene single crystal/SiO$_2$/doped Si dual-gate structure shown in Fig. 2, replacing polymer gel electrolyte with the IL based on our earlier study.[15] The channel dimensions between source and drain electrodes are w=100 μm in width and L=30 μm in length, which the droplet of the IL completely covers. A 25 μm thick gold wire

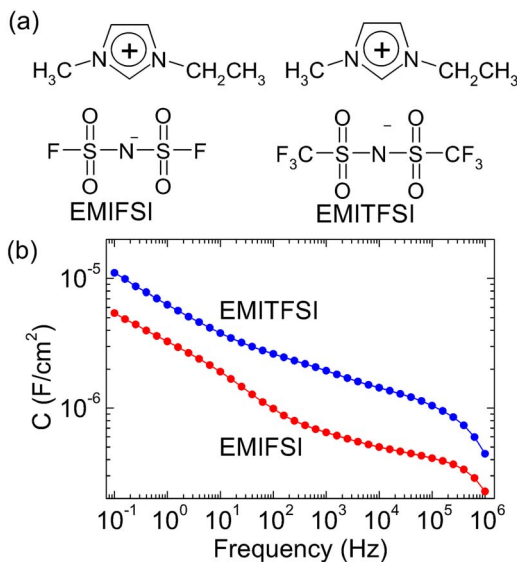a)Electronic mail: shimpei@criepi.denken.or.jp.

FIG. 1. (Color online) (a) Chemical structures of the ILs used in this device; EMIFSI (left) and EMITFSI (right). (b) Capacitance of the ILs as a function of frequency measured by the ac impedance technique.

is placed on the droplet in order to apply the gate voltage V_G, so that formation of the EDLs in the electrolyte can induce high-density carriers at the top surface of the crystal, while the gate voltage across the SiO$_2$ gate insulator induced carriers at the bottom surface for comparison.

The EDL capacitances C_{EDL} of the two ILs are measured using a test structure consisting of a 50 μm thick IL layer sandwiched by Au films. Solartron 1260 and 1296 impedance analyzers are used to obtain the frequency profiles over the range of 0.1 Hz$-$1 MHz with the application of ac voltage amplitude of 10 mV. As shown in Fig. 1(b), the values of the capacitance increase with decreasing frequency to reach 11 and 5.4 μF/cm^2 at 0.1 Hz for EMITFSI and EMIFSI,
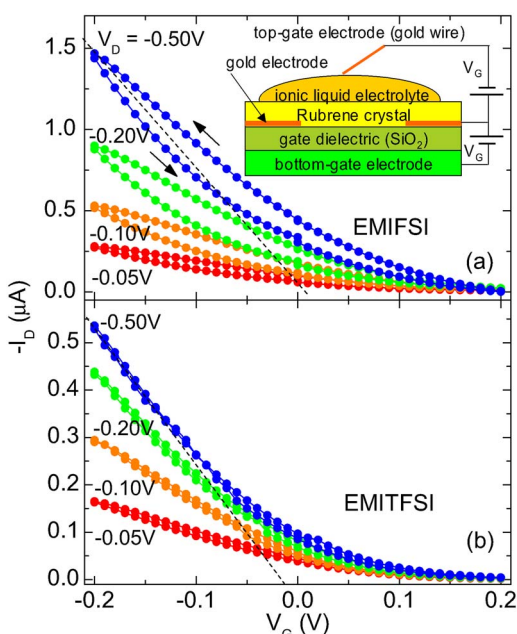

FIG. 2. (Color online) Transfer characteristics of the EDL OFETs with EMIFSI (a) and EMITFSI (b). The dotted lines are drawn to estimate the hole mobility μ of the devices. The arrows indicate the direction of the sweeps. The inset shows a schematic illustration of the dual-gate rubrene single crystal field-effect transistor with ionic liquid electrolyte.
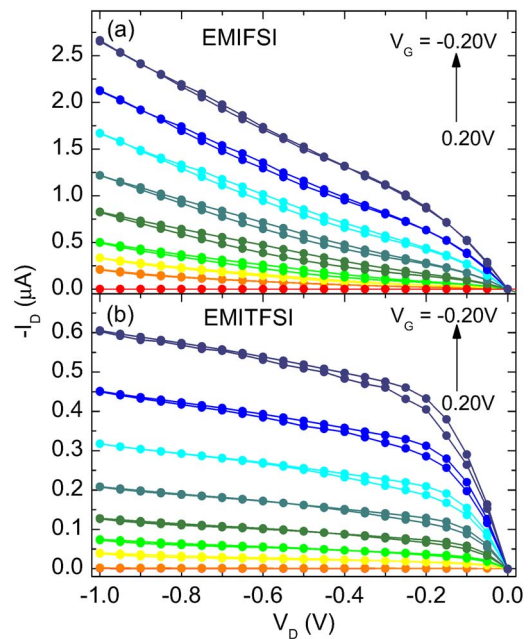

FIG. 3. (Color online) Output characteristics of the devices with EMIFSI (a) and EMITFSI (b) with different gate voltages (V_G =0.20, 0.15, 0.10, 0.05, 0.00, −0.05, −0.10, −0.15, −0.20 V, respectively).

respectively. If we assume the thickness of the EDLs to be typical length scales of the ionic molecules, the dielectric constant ϵ_{el} would be $\sim$13 and 6.3 for EMITFSI and EMIFSI, respectively. The values are close to those reported for polymer electrolytes.[15–17] Though the reason of the frequency dependence in the range of 0.1–10 Hz has not been elucidated yet, it is suspected that the rotational rearrangement of the ionic molecules is responsible for the observation of the slow relaxation. As a consequence of such high values of the EDL of EMITFSI, application of the gate voltage of 0.5 V leads to the carrier density as high as $\sim$1.0 $\times 10^{13}$/cm^2, which is comparable to the maximum carrier density that the usual SiO$_2$ devices can reach. It is to be emphasized that the EDL capacitance of the ILs remain large even at 1 MHz; the value is only one order of magnitude lower than that at 0.1 Hz for the both compounds, demonstrating the fast ionic diffusion in response to the voltage application. Therefore, the EDL OFETs incorporating the ILs allow switching operation at such a high frequency, which none of the previously reported devices with polymer electrolytes do.

Figures 2(a) and 2(b) show transfer characteristics of the device with EMIFSI and EMITFSI, respectively. Simultaneously measured gate leakage current through the electrolytes is negligibly small as compared to the drain current I_D, that is less than 0.1 nA as long as $|V_G|$ is less than 0.2 V. A sweeping rate of 0.01 V/s results in relatively small hysteresis for EMITFSI while a noticeable hysteresis is observed for EMIFSI between forward and reverse sweeps. Since the ac impedance in Fig. 1(b) does not show additional relaxation for EMIFSI as compared to that for EMITFSI, the different dynamic response comes from interfacial characters at the EMIFSI/rubrene crystal boundaries such as of hole-trapping levels possibly due to impurities in the IL or inclusion of water from atmosphere.

Figure 3 shows output characteristics of the rubrene crystal FETs with the two IL electrolytes. It is again notice-

able that rather large current in the order of microampere is generated with the application of less than 1 V for both V_G and V_D, demonstrating the very low-power operation of the organic transistors due to the high density carrier accumulation at the IL/rubrene liquid-to-solid interfaces. With increasing drain voltage V_D, a good saturating behavior is observed for the EMITFSI devices, while the saturation is not obvious for the EMIFSI devices. Such nonsaturative characteristics are often observed for high-mobility OFETs based on rubrene single crystals and pentacene thin films,[7,24] indicating that typical narrow pinch-off regions are not defined in the semiconductor channel of these devices. Since the reasons have not been argued well, it is to be elucidated by further experimental studies with devices of various channel lengths.

The hole mobility μ is estimated from the transfer characteristics by employing the standard formula in the Ohmic regime $\mu = I/w/1/C_{EDL}V_D/\partial I_D/\varepsilon V_G$. The dotted line in Fig. 2 shows the actual fit to the data to estimate μ. The obtained μ is in the range of 0.15–0.41 cm^2/V s for the EMITFSI devices and 0.58–1.2 cm^2/V s for the EMIFSI devices, as a statics of several similarly prepared samples. Though the values are already higher than those ever reported for EDL-gated FETs, we note that the mobilities can still be underestimated because of the inclusion of high-resistance "vertical" current paths between the gate and source (drain) electrodes. Mobility of the SiO$_2$ devices is estimated to be in the range of 0.6–1.5 cm^2/V s as the result of the same measurements of the transfer characteristics for the same conduction channel in the rubrene single crystals on the other side. Since the mobility values for the EDL transistors are comparable to those for the SiO$_2$ devices, the ILs provide efficient coupling to the organic single crystals without sacrificing carrier mobility at the solid/liquid interface between organic semiconductors and the ILs.

As for the difference in μ of the two ILs, it can be argued that the surface charge is dressed with differently polarizable gate dielectrics. Although the effect of the liquid electrolytes should be different from that of solid gate insulators, the present results qualitatively follow the tendency that μ increases with gate insulators of smaller ϵ as reported for carriers on common dielectric insulators.[25,26] On the other hand, Shimotani *et al.* explain that the scattering events of the carriers by the ion are relevant in the electrolyte.[17] Including our present results on the IL/rubrene semiconductor interfaces, it is to be further investigated to elucidate microscopic mechanisms of the charge transport in the vicinity of the solid/liquid interfaces.

In conclusion, it is demonstrated that the use of IL electrolytes in organic single-crystal FETs enable high-density carrier doping with minimum gate voltages without sacrificing the carrier mobility. Therefore, the IL gating can be a promising technology to realize high-mobility, fast-switching, and low-power organic transistors. Owing to varieties of ILs that have been synthesized so far, higher performances are likely to emerge by elaborate search for compounds incorporated in organic FETs. Due to the capability of the high density carrier doping, the present technique is also useful in more basic material sciences such as carrier-density driven phase transition in strongly correlated electron systems.

[1] G. Malliaras and R. Friend, Phys. Today **58**, 53 (2005).
[2] V. Podzorov, V. M. Pudalov, and M. E. Gershenson, Appl. Phys. Lett. **82**, 1739 (2003).
[3] J. Takeya, C. Goldmann, S. Haas, K. P. Pernstich, B. Ketterer, and B. Batlogg, J. Appl. Phys. **94**, 5800 (2003).
[4] R. W. I. de Boer, T. M. Klapwijk, and A. F. Morpurgo, Appl. Phys. Lett. **83**, 4345 (2003).
[5] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, and J. A. Rogers, Science **303**, 1644 (2004).
[6] J. Takeya, J. Kato, K. Hara, M. Yamagishi, R. Hirahara, K. Yamada, Y. Nakazawa, S. Ikehata, K. Tsukagoshi, Y. Aoyagi, T. Takenobu, and Y. Iwasa, Phys. Rev. Lett. **98**, 196804 (2007).
[7] C. Reese, W.-J. Chung, M.-M. Ling, M. Roberts, and Z. Bao, Appl. Phys. Lett. **89**, 202108 (2006).
[8] M. Uno, Y. Tominari, and J. Takeya (unpublished).
[9] J. Takeya, K. Tsukagoshi, Y. Aoyagi, T. Takenobu, and Y. Iwasa, Jpn. J. Appl. Phys., Part 2 **44**, L1393 (2005).
[10] V. Podzorov, E. Menard, J. A. Rogers, and M. E. Gershenson, Phys. Rev. Lett. **95**, 226601 (2005).
[11] J. Kraitchman, J. Appl. Phys. **38**, 4323 (1967).
[12] M. Halik, H. Klauk, U. Zschieschang, G. Schmid, C. Dehm, M. Schütz, S. Maisch, F. Effenberger, M. Brunnbauer, and F. Stellacci, Nature (London) **431**, 963 (2004).
[13] M. J. Panzer, C. R. Newman, and C. D. Frisbie, Appl. Phys. Lett. **86**, 103503 (2005).
[14] M. J. Panzer and C. D. Frisbie, Appl. Phys. Lett. **88**, 203504 (2006).
[15] J. Takeya, K. Yamada, K. Hara, K. Shigeto, K. Tsukagoshi, S. Ikehata, and Y. Aoyagi, Appl. Phys. Lett. **88**, 112102 (2006).
[16] E. Said, X. Crispin, L. Herlogsson, S. Elhag, N. D. Robinson, and M. Berggren, Appl. Phys. Lett. **89**, 143507 (2006).
[17] H. Shimotani, H. Asanuma, J. Takeya, and Y. Iwasa, Appl. Phys. Lett. **89**, 203501 (2006).
[18] M. J. Panzer and C. D. Frisbie, J. Am. Chem. Soc. **129**, 6599 (2007).
[19] J. Lee, M. J. Panzer, Y. He, T. P. Lodge, and C. D. Frisbie, J. Am. Chem. Soc. **129**, 4532 (2007).
[20] R. Misra, M. McCarthy, and A. F. Hebard, Appl. Phys. Lett. **90**, 052905 (2007).
[21] M. A. B. H. Susan, T. Kaneko, A. Noda, and M. Watanabe, J. Am. Chem. Soc. **127**, 4976 (2005).
[22] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, N. Kihira, M. Watanabe, and N. Terada, J. Phys. Chem. B **110**, 10228 (2006).
[23] S. Seki, Y. Ohno, H. Kobayashi, H. Miyashiro, A. Usami, Y. Mita, H. Tokuda, M. Watanabe, K. Hayamizu, S. Tsuzuki, M. Hattori, and N. Terada, J. Electrochem, Society **154**, A173 (2007).
[24] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, and W. Weber, J. Appl. Phys. **92**, 5259 (2002).
[25] A. F. Stassen, R. W. I. de Boer, N. N. Iosad, and A. F. Morpurgo, Appl. Phys. Lett. **85**, 3899 (2004).
[26] I. N. Hulea, S. Fratini, H. Xie, C. L. Mulder, N. N. Iossad, G. Rastelli, S. Ciuchi, and A. F. Morpurgo, Nat. Mater. **5**, 982 (2006).