Thema

Improvement of properties of gate insulators for low voltage operating organic thin film transistors

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1. Introduction

Flexible electronics on polymer substrates require device structures that are amendable to room temperature fabrication and processing[1,2]. Organic thin film transistors (OTFTs) based on pentacene satisfy this criteria. OTFTs have received intense interest for applications requiring, structural flexibility, large area coverage, and low-cost. Such applications include active matrix OLED/LCD displays, sensing devices, and radio frequency identification (RFID) tags[3-6]. To obtain low voltage operation (a requirement for low power electronic systems) and high performance (i.e. high mobility), OTFTs often require the use of high capacitance gate insulator suitable for portable, battery-powered device applications. High capacitance gate insulators can be obtained by the use of very thin films and/or high dielectric constant gate materials. Very thin gate insulators can lead to significant manufacturing problems given that the surface roughness of the polymers may be on the order of the thickness of the insulators leading to pinholes in the insulator, and high resultant leakage currents. Flexible polymer substrates, often characterized by rough surfaces (RMS roughness ~ 3 nm), therefore benefit from the use of high-K dielectrics given that high electric fields can be achieved with use of thicker films (~ 200 nm) without need to increase operating voltage. Further, room temperature processing could enable 3D integration of large stacks of active electronic device layers as well as flexible/wearable electronics, and conformable 3D imaging.

In addition, transparent thin film transistors (TTFTs), represented by ZnO-based TFTs which can be processed at room temperature have attracted much attention due to their potential of replacing hydrogenated amorphous or polycrystalline silicon (a-Si:H or poly-Si) TFTs. ZnO is a transparent compound semiconductor with a wide band gap (3.37 eV) which can be grown as a polycrystalline film at room temperature.

Therefore, ZnO is considered to be an ideal material for serving as the channel layer in transparent and flexible TFTs because invisible ZnO-TFTs offer higher aperture ratio for the transmission of backlight in flat panel displays. So far, considerable efforts have been done to obtain high performance ZnO (or doped ZnO)-TFTs with high field-effect mobility (1 ~ 80 cm^2/Vs) and high on/off ratios (10^5 ~ 10^7). However, large threshold and high operating voltages are still a major limitation for portable, battery-powered applications. In order to drive higher operating current at lower bias voltages, high-K gate dielectrics of more than 200 nm thickness (pinhole-free and good step coverage) are normally needed to increase the capacitive coupling of the gate electric field to the ZnO channel layer[7].

Therefore, in this article, we will discuss and focus on the methods to obtain low voltage operating OTFTs by using more improved gate dielectrics modified by simple techniques which play an important role in modern OTFTs technologies.

2. Main subject

2.1 Basic characteristics of FETs (Field Effect Transistors)

Fig. 1 shows a general FET comprising three electrodes (gate(G), source(S), and drain(D)), a dielectric layer, and a semiconducting layer. When a gate voltage is not applied on G, FET device is in an 'off' mode between S and D. While a gate voltage is applied on G, an "active channel" of a current between S and D is formed(an 'on' mode). By the nature of the semiconductor and electrodes utilized on the FET, the channel formed can be an n-type FET(electrons are the carriers) or a p-type FET(holes are the carriers). The characteristics of the FET is measured by the mobility (μ) of charges in the semiconductor and D-S current ratio between on and off modes. μ higher than 0.1 cm^2/Vs and on/off ratios higher than 10^6 are desirable for practical application of FETs in circuits. μ of organic semiconductors depends on the degree of overlapping of charge-accepting orbitals of neighboring molecules. Organic semiconductors are relevant to weak Van der Waals interaction among discrete molecular elements for charge transports, on the contrary to inorganic semiconductors. Manufacturing FETs consisting of organic compounds with good performances claims a drastic comprehension of the charge movements in these systems.

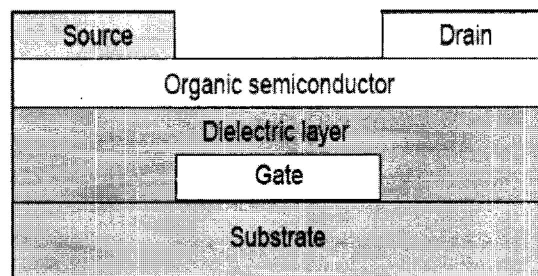


Fig. 1. Schematic diagram of FET.

2.2 Insulators - Inorganic materials

Considering the various flexible TFT structures, it becomes immediately evident that for the manufacture of high-quality flexible TFTs, the semiconductor is not the only critical component. It is also very important to incorporate a suitable gate insulator. The crucial parameters are the maximum possible electric displacement D_{max} the gate insulator can sustain,

$$D_{max} = \varepsilon_0 k E_B$$

where k is the dielectric constant, E_B is the dielectric breakdown field; and the capacitance per area C_i is

$$C_i = \varepsilon_0 (k/d)$$

with d as the insulator thickness. The capacitance magnitude is governed not only by the k value but also by the thickness (d) for which a pin-hole free film can be achieved, and thus may reflect the deposition procedure as well as intrinsic materials properties.

The major motivation to search for SiO_2, the most-ever used insulator (k=3.9), alternatives is to significantly reduce the flexible TFT operating voltage. In fact, while carrier mobilities of semiconductors have now approached or surpassed those of amorphous Si, this has generally been achieved at very large source-drain or source-drain biases, typically greater than 30-50 V. Flexible TFT operation employing such large biases will incur excessive power consumption. No wonder the driving force for high-k insulators is the need to increase TFT density on integrated circuits while preserving good insulator properties. Pentacene TFTs have demonstrated the highest performance among TFTs with an organic semiconductor channel. High operating voltages (20-100 V), stemming from poor capacitive coupling between gate electrode and channel are a major limitation, particularly for portable, battery-powered device applications. A combination of higher permittivity gate dielectric and reduced dielectric thickness leads to lower voltage operation. However, flexible TFTs with thin gate dielectrics showed much poorer performance on flexible polymer substrates, often characterized by rough surfaces, making TFTs susceptible to pinhole formation and low manufacturing yields. In order to realize flexible TFT technologies on polymer substrates with relatively high surface roughness (~ 3 nm), low leakage, high-K gate dielectrics capable of being

Table 1. Summary of the dielectric and OTFT characteristics for various inorganic gate dielectrics.

Ref.	Dielectric	Method [a]	D [nm]	C_i [nF cm^{-2}]	k	E_B [MV cm^{-1}]	Semicond.	μ [cm^2 V^{-1} s^{-1}]	I_{on}/I_{off}	Year
19	BZT	sputt.	122		17.3		Pentacene	0.32	10^5	1999
	BST				16		Pentacene	0.4–0.5		
	Si_3N_4				6.2		Pentacene	0.6		
20	Ta_2O_5	anodiz.	70		23	4–5	DH-5T	–0.03		2000
							FPcCu	–0.02		
21	Ta_2O_5	e-beam	100	180	21	>1	P3HT	–0.2		2002
24,25	Al_2O_{3+x}	sputt.	270	22	7	-3	Pentacene	0.14	10^6	2003
26	Al_2O_3	anodiz.	120	60		-8	PTAA	3×10^{5}		2003
22	Ta_2O_5	anodiz.	86	248	24		Pentacene	0.24	10^4	2003
23	Ta_2O_5	sputt.		66			PcCu	0.01		2003
24	SiO_x	PECVD					Pentacene	0.2–0.4	~10^8	2003
	SiN_x									
30	TiO_2	sputt.	97	373	41	-3	P3HT	5×10^{3}	10^2	2004
	Al_2O_3		93	79	8.4	-8	P3HT	6×10^{-3}	10^2	
27	Al_2O_3	anodiz	–7	600–700	9–11		P3HT	$1.1–1.4\times10^{-3}$		2004
							Pentacene	0.06–0.1		
32	Ta_2O_5–air	sputt.			25–1		Rubrene	1.5–20		2004
33	Gd_2O_3	IBDA	90	280	7.4		Pentacene	0.1	10^3	2004
31	TiO_2+PαMS	anodiz.	8+10	228			Pentacene	0.8	10^4	2005

prepared at or near room temperature are essential. Thin dielectric layers, deposited on, for example, rough polyimide substrates, may result in the formation of pinholes and, in turn, increased leakage. The use of appropriate high-k materials would afford comparable or greater capacitance values, and therefore semiconductor-dielectric interface at greater insulator thickness with lower leakage currents[7]. Naturally a great number of efforts have been made to lower the operating volatage of flexible TFTs using high-k materials. Table 1 shows important metrics for the inorganic dielectrics and OTFTs. Polymer insulators have been also developed by various kinds of groups, but their dielectric constants are much lower than those of inorganic insulators[7]. Therefore, inorganic insulators might be the best insulators for the flexible TFTs.

2.3 Pentacene TFTs with 3 % Mn-doped BST thin films gate insulators

Dimitrakopoulos *et al.* reported low voltage operating OTFTs using room temperature deposited (Ba,Zr)TiO_3 (BZT) and (Ba,Sr)TiO_3 (BST) thin films with relative dielectric constants of 17.3 and 16 respectively as gate dielectrics[8]. However, BST films of thickness less than 200 nm suffer from relatively high leakage current densities, and need annealing at 400 °C after deposition, unsuitable for OTFTs application. Recently, BST thin films modified by the perovskite B-site acceptor were studied for microwave tunable device application given their low dielectric loss tangent (tan δ) in the microwave frequency regime[9]. Kang et al[10,11]. have applied this fact to the room-temperature deposited BST thin films to acquire decreased leakage current properties using Mn as an acceptor. Fig. 2 shows a schematic diagram of an OTFTs structure. Fig. 3 and 4 show electrical characteristics of BST thin films and TFTs. The 3 % Mn-doped BST

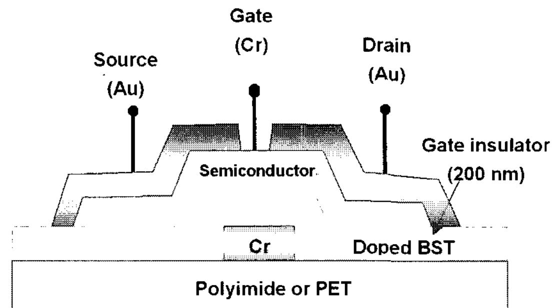
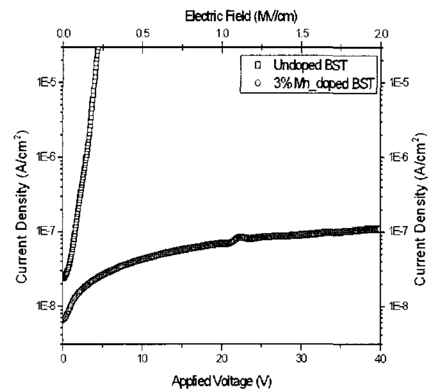


Fig. 2. Schematic diagram of OTFTs structure.



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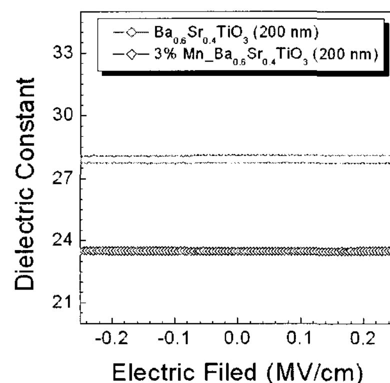
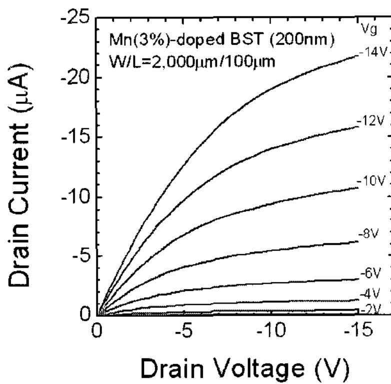


(b)

Fig. 3. Electrical characteristics of undoped and 3 % Mn-doped BST thin films grown on Pt electrodes at room temperature.

thin film by sputtering showed a relatively high dielectric constant of 24 with much reduced leakage current characteristics, i.e. less than 10^{-7} A/cm^2 at an applied voltage of 5 V as compared to undoped BST. High breakdown strength was observed up to 2 MV/cm. Pentacene TFTs, operating at reduced voltage (< 10 V), were successfully fabricated using the high-K 3 % Mn-doped BST gate dielectrics. Threshold voltage and field effect mobility were -1 V and 0.32 cm^2/Vs, respectively.



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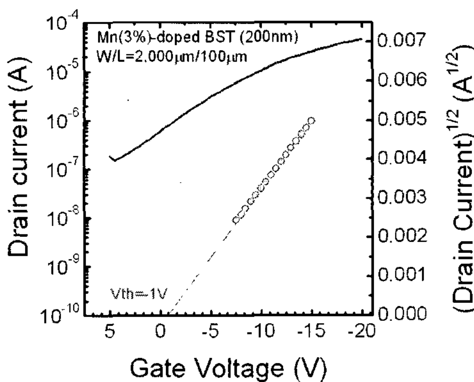


(b)

Fig. 4. TFT characteristics of the 3 % Mn-doped BST thin film used the pentacene OTFT.

2.4 ZnO-TFTs with 3 % Mn-doped BST thin films gate insulators on plastic substrates

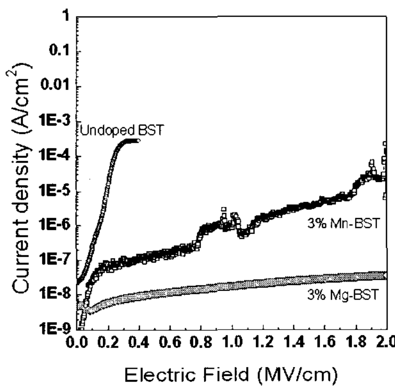
Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films have excellent properties as a gate insulator deposited at room temperature. The films could provide the requisite high dielectric constant (~ 24) coupled with enhanced leakage current characteristics. However, Mn, which occupies the Ti site (Ti^{4+}, r_{eff}=0.605 Å) of the (Ba,Sr)TiO_3 perovskite structure, has multi-valence states with ionic radii between Mn^{2+} (r_{eff}=0.67 Å) and Mn^{4+} (r_{eff}=0.53 Å) in a six-fold coordination[7]. If an electron acceptor with lower single valence state, i.e., Mg^{2+} (r_{eff}=0.72 Å) is used, further reduction in the leakage current density can be achieved due to the deep trapping of electrons that would be normally generated in the Ti derived 3-d-like conduction band[11]. Fig. 5 and 6 show electrical characteristics of BST thin films and TFTs. 3% Mg-doped BST films with a high dielectric constant (ε_r ~22) and low leakage current property (< ~ 5 x 10^{-8} at 2 MV/cm) were prepared at room temperature by sputtering. A remarkable reduction in leakage current density could be achieved through deep trapping of electrons that would be normally generated in the Ti derived 3-d-like conduction band. All room temperature processed ZnO-TFTs on PET substrates using the 3 % Mg-doped BST gate insulators (200 nm) exhibited low voltage operation of less than 6 V and a high field effect mobility of 16.3 cm^2/Vs. The results of this work indicate that 3 % Mg-doped BST gate insulators are essential for producing low voltage ZnO-TFTs with high field effect mobility toward future flexible electronics.

2.5 Acceptor doping effect

BST is a promising ferroelectric material for tunable microwave device applications such as electronically tunable mixers, delay lines, filters, and phase shifters. But, as it has high dielectric loss,

considerable efforts have been made to increase the tunability through the control of thin films and orientation and decrease the dielectric loss of tunable thin films by dopant addition[7]. It is well documented that small concentrations of dopants can dramatically modify the properties of ferroelectric materials such as BST. In particular, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Mg^{2+}, Al^{2+}, Ga^{3+}, In^{3+},Cr^{3+}, and Sc^{3+}, which can occupy the B sites of the ($A^{2+}B^{4+}O_3^{2-}$) perovskite structure, have been known to lower dielectric loss and leakage current. Fig. 7 shows a schematic structure for acceptor substitution into Ti site in BST lattice. The mechanism for this behavior centers on the thesis that ions with a charge less than 4+ can substitute for Ti^{4+} and behave as electron acceptors[10,11].

Doping of acceptors to BST is also known to increase Schottky barrier heights and results in decrement in leakage current density[7]. In addition, X. Wang et al. suggested that doping with Mn is one of several ways to confine the electrons to



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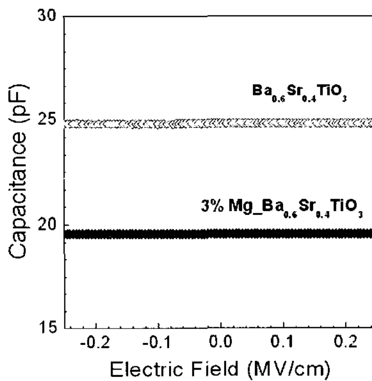
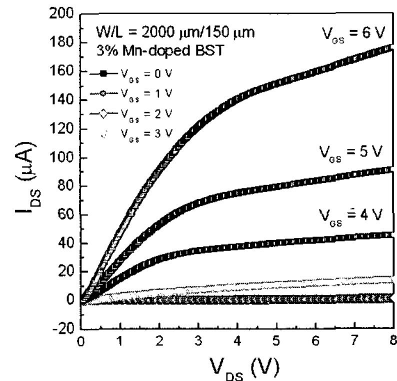


(b)

Fig. 5. Electrical characteristics of undoped and 3 % Mg-doped BST thin films grown on Pt electrodes at room temperature.



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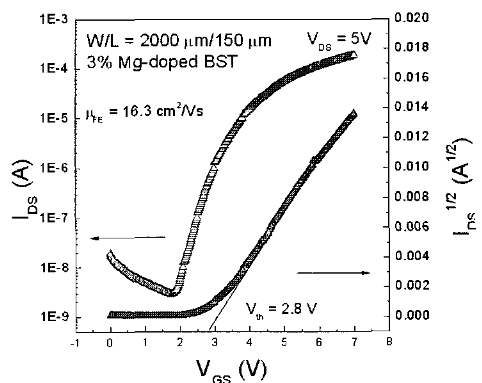


(b)

Fig. 6. TFT characteristics of the ZnO-based TFTs on PET using 3 % Mg-doped BST thin films.

a small region. In Mn-doped $BaTiO_3$, there exist three valence states for the manganese ions, Mn^{2+}, Mn^{3+} and Mn^{4+}. The Mn^{4+} is nearly exactly incorporated into Ti sites and participates in the collective motion in the lattice[7].

When some titanate sites are occupied by Mn ions at the valence 3+ or 4+, the electrons will be trapped on these sites because Mn^{3+} and Mn^{4+} are more reducible than the Ti^{4+}.

Because the Mn concentration is very low, the hopping motion of the trapped electrons from one Mn site to another is almost impossible. In other words, the electrons are effectively localized on these Mn sites. Therefore, doping with Mn into $BaTiO_3$ would reduce the conductance of $BaTiO_3$ ceramics. Plus, Mn is intentionally added to $BaTiO_3$-based multilayer-ceramic capacitors (MLCC) with base metal (Ni) electrodes in order to keep $BaTiO_3$ from reducing and becoming leaky when sintering under reducing conditions[7].

From above reports, although there are no reports on the characteristics of room temperature deposited Mn-doped BST thin films, it could be thought that Mn acceptor plays an important role to decrease the electron density, the source of leakage current, and increase Schottly barrier heights. Also, it is attributed to the deep Mn acceptor level (~1.69 eV above the valence band) that Mn^{4+} occupies within the band gap of $BaTiO_3$ (~2.9-3.0 eV) thereby trapping electrons that would otherwise normally be generated in the Ti derived 3d-like conduction band. Likewise, on the basis of the similar ionic radii between Ti^{4+} (r_{eff}=0.605 Å) and Mn^{4+} (r_{eff}=0.53 Å) in sixfold coordination, it can be assumed that Mn also occupies Ti sites in the BST lattice. Indeed, Mn has been found to lower the dielectric loss in BST films[10]. This Mn induced decrease in electron density is also expected to be the source of reduced leakage currents in Mn-doped BST films[7].

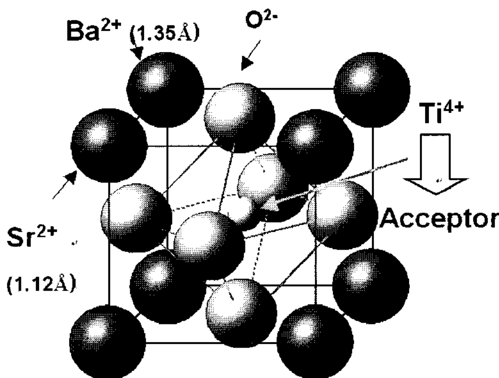
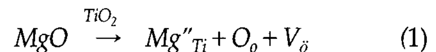


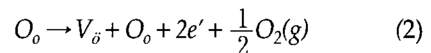
Fig. 7. Schematic structure for acceptor substitution into Ti site in BST lattice.

In case of Mg doping, on the basis of the similar ionic radii between Ti^{4+} (r_{eff}=0.605 Å) and Mg^{2+} (r_{eff}=0.72 Å) in the six-fold coordination, we assume that Ti^{4+} can be replaced by Mg^{2+}. Negatively charged defects (Mg''_{Ti}) and a corresponding number of doubly ionized oxygen vacancy ($V_{\ddot{o}}$) is simultaneously formed to satisfy the site balance and charge neutrality.



$$MgO \xrightarrow{TiO_2} Mg''_{Ti} + O_o + V_{\ddot{o}} \qquad (1)$$

In this case, Mg behaves as an acceptor-type dopant and can prevent reduction of Ti^{4+} to Ti^{3+} by neutralizing the donor action of the oxygen vacancies. During the BST film growth, a reduction process may result in n-type conductivity in the prepared films according to the following equation.



$$O_o \rightarrow V_{\ddot{o}} + O_o + 2e' + \frac{1}{2}O_2(g) \qquad (2)$$

Where O_o, $V_{\ddot{o}}$, and e' represent the oxygen ion on its normal site, the oxygen vacancy, and electron, respectively. The increase in the oxygen vacancy concentration created by MgO addition eventually causes a decrease in the concentration of electrons. This decrease in electron density can lead to lower

leakage current in BST films. In accordance with these arguments, the leakage current density of Mg-doped BST film was markedly reduced as compared to that of intrinsic BST film and that of 3 % Mn-doped BST, as shown in Fig. 30. Although 3 % Mg-doped BST films showed non-crystalline structure in SEM morphology, but it is expected to have local short-range ordering in 3 % Mg-doped BST films[11]. Therefore, the defect notation which was described by simple substitution of Mg^{2+} for Ti^{4+} in equations (1) and (2) might be used to explain the remarkable reduction of leakage current density. To confirm this can be acceptable and to investigate the existence and valence stage of Mg dopants in the BST matrix, X-ray photoelectron spectroscopy (XPS) was carried out and the Mg 1s spectra in XPS was observed shown in Fig. 8. These results indicate that Mg was well doped within the BST matrix. For Mg 1s spectra in XPS, the peak position was recorded in a range of 1303.5-1304.1 eV. The corresponding Mg-O peak position for Mg 1s is 1303.8 eV. The peak position is well matched with the measured Mg 1s peak position. This indicates that Mg could serve as an electron acceptor in the BST matrix with chemical bonding of Mg-O to lower leakage current density.

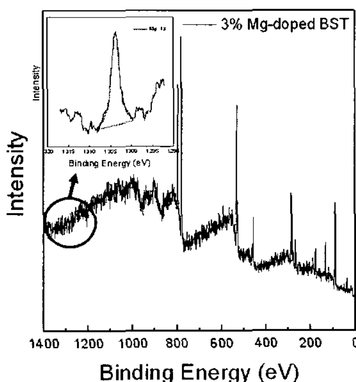


Fig. 8. XPS spectra for Mg 1s peak.

Therefore, acceptor doping to BST might serve as a milestone for realizing flexible electronics and their use in portable and battery-powered applications.

3. Conclusion

OTFTs have been investigated for use in low-cost, large-area, flexible electronic applications. There are many factors to improve properties of OTFTs such as organic semiconductors, substrates and electrodes etc. In here, we have focused on improving properties of gate dielectrics which play an important role in low voltage operation, realizing portable and battery-powered applications of OTFT-based devices. Like mentioned here, if simple methods such as doping introduced here are devised for developing OTFTs, application fields of OTFTs will be broadened, which might realize imaginary things seen on science fictions and movies such as A Space Odyssey.

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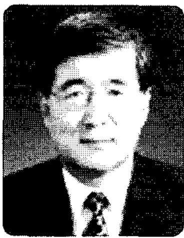

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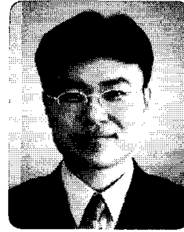

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