Pentacene-Based Thin-Film Transistors With a Solution-Process Hafnium Oxide Insulator

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***Abstract*—Pentacene-based organic thin-film transistors with solution-process hafnium oxide (HfO_x) as gate insulating layer have been demonstrated. The solution-process HfO_x could not only exhibit a high-permittivity ($\kappa = 11$) dielectric constant but also has good dielectric strength. Moreover, the root-mean-square surface roughness and surface energy (γ_s) on the surface of the HfO_x layer were 1.304 nm and 34.24 mJ/cm^2, respectively. The smooth, as well as hydrophobic, surface of HfO_x could facilitate the direct deposition of the pentacene film without an additional polymer treatment layer, leading to a high field-effect mobility of 3.8 $cm^2/(V \cdot s)$.**

***Index Terms*—Hafnium oxide, high permittivity, organic thin-film transistor (OTFT), solution process, surface energy.**

I. INTRODUCTION

ORGANIC thin-film transistors (OTFTs) have drawn extensive attention for their applications in radio-frequency rectifiers, chemical sensors, and integrated circuits. The characteristics of pentacene-based thin-film transistors with a mobility of 1.5 $cm^2/(V \cdot s)$ have been reported [1]. They were found to approach the level of hydrogenated amorphous silicon (a-Si:H) TFTs [2]. However, a reduction of operating voltage for OTFTs can be achieved through increasing capacitance density by using a high-permittivity inorganic metal–oxide gate insulator or by reducing the thickness of the gate insulator. In addition, typical high-κ inorganic metal–oxide gate insulators cannot only be thick to prevent serious gate leakage current but also maintain the same level of capacitance density.

A number of high-permittivity inorganic metal–oxide materials, such as tantalum oxide [3], titanium oxide [4], magnesium oxide [5], and hafnium oxide [6], have been widely studied. Among these different materials, hafnium oxide is a promising candidate due to its larger bandgap than other high-permittivity competitors [7]. However, most high-permittivity inorganic metal–oxide films have been deposited by sputtering [3], [4] or electron-beam evaporation [6] under a vacuum system. In addition, most high-κ materials are based on ceramics, which are fragile and are not suitable for flexible and large-area electronics [8]. In this letter, the solution-processed HfO_x film will be demonstrated by spin coating under a low-cost deposition system. The simple transistor structure, good performance, and the absence of any surface treatments would be applicable for large-area or ink-jet electronic technology. The corresponding physical and electrical properties of the HfO_x as the gate insulating layer of OTFTs will be investigated.

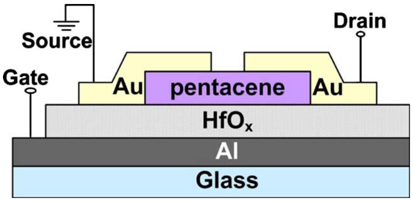

Fig. 1. Cross-sectional schematics of the pentacene-based TFTs. The thickness of HfO_x was 190 nm, which was measured by the Alpha step.

II. DEVICE STRUCTURE AND FABRICATION

The cross-sectional schematic of top contact pentacene-based TFTs is shown in Fig. 1. Aluminum (Al) was deposited by RF sputtering through a shadow mask to form the gate electrode on the Corning glass Eagle^{2000} substrate. Hafnium oxide solution was prepared by mixing 4.96-g hafnium dichloride oxide octahydrate, $98^{+}\%$ (40 wt% from Alfa Aesar) with 1-g glycine (8 wt%), and 3.6 ml of deionized (DI) water; then, it was boiled to dissolve the solutes under the airtight space. Subsequently, the limpid solution at room temperature was done by adding 2.95-ml DI water and then spin coated onto the Al/glass substrate to form a transparent insulating layer. Finally, the sample was baked on a hot plate at 200 °C for 30 min under ambient air condition, and the thickness of the gate insulating layer was 190 nm, as determined by an Alpha-step surface profiler. Pentacene was thermally evaporated on the insulating layer at a deposition rate of 0.08 nm/s. The gold electrode patterns were finally deposited by RF sputtering as the source and drain, and the channel length (L) and width (W) were 150 and 1500 μm, respectively.

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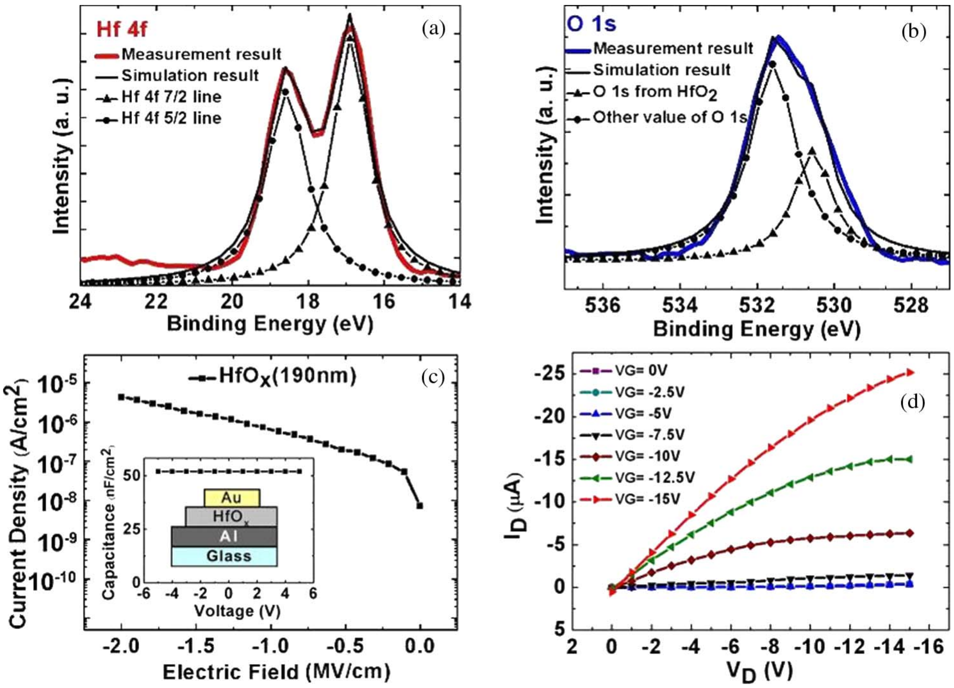

Fig. 2. XPS core level spectra of (a) Hf $4f$ and (b) O $1s$ emissions from the HfO$_x$ thin film cured at 200 °C for 30 min under ambient air condition. (c) Leakage current density versus applied electric field (J–E) and capacitance density versus applied voltage (C–V) characteristics were plotted from the metal–oxide–metal ($\mathrm{Al-HfO}_x\mathrm{-Au}$) structure. (d) Current–voltage characteristics (I_D–V_D) for a pentacene-based OTFT with a 190-nm-thick HfO$_x$ insulator.

The electrical characteristics of the transistor were measured by the semiconductor parameter analyzer HP 4156B under atmospheric condition at room temperature. The chemical composition and binding energy of the HfO$_x$ film were analyzed by X-ray photoelectron spectroscopy (XPS).

III. IMPLEMENTATION AND PERFORMANCE

Fig. 2 shows the Hf $4f$ and O $1s$ emission spectra from the spin-coated HfO$_x$ layer. Fig. 2(a) shows the doublet feature in the range between 16 and 20 eV, which is spin splitting of 16.87 and 18.6 eV. Such phenomena may be due to the splitting of Hf $4f$ 7/2 and 5/2 spin states and indicates the formation of energy of the Hf–O bonds. In addition, the theoretical value of the O $1s$ peak binding energy from HfO$_2$ is 530.4 eV [9]. The other chemical state of O $1s$ at 531.8 eV from our sample, as shown in Fig. 2(b), is probably due to the moisture and hydroxyl groups under the atmosphere environment [10]. A good agreement between the simulation results composed of two different O $1s$ states with the measurement data can be observed. By using the XPS data, the ratio between O and Hf with a value of $x = 4.58$ can be obtained.

Fig. 2(c) shows the leakage current density (J_L) as a function of the applied electrical field of the metal–insulator–metal $(\mathrm{Al-HfO}_x\mathrm{-Au})$ structure. The capacitance of the HfO$_x$ layer was measured through HP 4280A measurement under 1 MHz, as shown in the inset of Fig. 2(c). According to the capacitance data, the dielectric constant κ was estimated to be about 11.16. As compared to other processes, the lower value of the dielectric constant may be attributed to the loose structure that has a lot of moisture during the solution process. However, the leakage current density of the spun HfO$_x$ with a dielectric strength of 4.36×10^{-6} A/cm^2 at an electric field of -2 MV/cm can be seen. The leakage current density is still high and needs further improvement. The integrity of looser solution-processed dielectrics can be improved by annealing at higher temperature to make the device reliable.

Fig. 2(d) shows the current–voltage characteristics at different gate–source voltages (V_G) from 0 to -15 V for pentacene-based OTFTs with a HfO$_x$ single-layer gate insulator. When the V_G is biased at -12.5 V, an output drain current (I_D) of -15 μA can be obtained. In addition, the threshold voltage (V_T) is -7.46 V. The on/off current ratio is about 10^2 from -15 and 0 V of gate bias at $V_{\mathrm{DS}} = -10$ V [11]. This low value may partly be attributed to the loose dielectric structure by the solution process. A subthreshold slope swing (*SS*) of 2.6 V/dec is obtained. The linear field-effect mobility is about $0.6\ \mathrm{cm}^2/(\mathrm{V} \cdot \mathrm{s})$. According to a published paper [12], the field-effect mobility could be calculated at the saturation region with a capacitance of 52 nF/cm^2. A saturation field-effect mobility of $3.8\ \mathrm{cm}^2/(\mathrm{V} \cdot \mathrm{s})$ is obtained when the V_G is biased at -10 V in the saturation region. Several published reports [5], [13] have indicated that the saturation mobility of pentacene film could be improved by the smoother surface roughness or the more hydrophobic surface of the insulator through treatment modification. In this letter, the smooth root-mean-square (rms) surface roughness and matching surface free energy of the HfO$_x$ layer could contribute to the superior saturation mobility without an additional treatment process, as discussed hereinafter.

The surface energies of the HfO$_x$ film were deduced by measuring the contact angles. The contact angles of DI water and di-iodomethane were 76.6° and 65.7°, respectively. With a combination with Young's formula and the equation derived by

TABLE I
COMPARISON OF THE PUBLISHED HIGH-κ MATERIALS WITH THAT OF THIS LETTER

Insulator (Process method)	On/off current ratio	J_L (A/cm^2)	κ	Rms (nm)	V_T (V)	SS (V/dec)	$\mu_{saturation}$ ($cm^2/(V\cdot s)$)	Ref.
Ta_2O_5 (Sputtering)	~10^2 when V_{GS}=0 ~ -10V at V_{DS}=-10V	~1.5×10^{-7} at E=0.34MV/cm	N/A	N/A	0.72	N/A	0.32	[3]
MgO (Evaporation)	~10^3 when V_{GS}=0 ~ -5V at V_{DS}=-5V	2.4×10^{-5} at E=0.24MV/cm	10.5^d	6.1	-2.67	N/A	0.66	[5]
$HfO_2{}^a$ (E-gun)	~10^2 when V_{GS}=0 ~ -15V at V_{DS}=-10V	~1×10^{-6} at E=0.6MV/cm	24.4^c	N/A	-0.1	2.1	0.1	[6]
$BaTiO_3{}^b$ (Solution)	~6×10^4 when V_{GS}=0 ~ -15V at V_{DS}=-10V	~1×10^{-8} at E=0.2MV/cm	14^d	8.81	-1.96	0.67	0.04	[13]
HfO_x (Solution)	~10^2 when V_{GS}=0 ~ -15V at V_{DS}=-10V	4.3×10^{-6} at E=2MV/cm	11.16^c	1.304	-7.46	2.6	3.8	This work

[a] *extracted from* $SCCO_2$*-treated* HfO_x. [b] *extracted from 37 vol % $BaTiO_3$ of the nanocomposite gate insulator.*
[c] *Measured at the frequency of 1 MHz.* [d] *Measured at the frequency of 1 kHz.*

Owens and Wendt [14], the surface energy of the HfO_x layer can be written as

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P}\left(\sqrt{\frac{\gamma_l^P}{\gamma_l^D}}\right) + \sqrt{\gamma_s^D} \qquad (1)$$

where γ_l^D and γ_l^P are the dispersion and polar terms of the liquid surface energy, which are 21.8 and 51.8 $\mathrm{mJ/m^2}$ for DI water while 50.8 and 0 $\mathrm{mJ/m^2}$ for di-iodomethane, respectively. γ_l is the total surface energy of the liquid, which can be obtained by adding the dispersion and polar terms. The surface energy of the HfO_x layer can be solved from (1) through the linear equation in two variables. Finally, the total surface energy of the inorganic HfO_x layer is 34.24 $\mathrm{mJ/m^2}$. According to the work of Drummy and Martin [15], the surface energy theoretical value derived for the orthorhombic-phase pentacene grown was 38 $\mathrm{mJ/m^2}$. This result is compatible with the polymer additional treatment layers, such as 39.7 $\mathrm{mJ/m^2}$ of poly(imide siloxane) [16] or 38.2 $\mathrm{mJ/m^2}$ of photosensitive polyimide [17]. Table I shows a comparison of the published high-κ materials with that of this letter. According to the definition of on/off ratio [11], the OFF current state was extracted at $V_{\mathrm{GS}} = 0$ for comparison. The large threshold voltage and subthreshold *SS* need further improvements. As to the surface roughness, effective saturation mobility, and dielectric strength, the proposed transistors are much better than those of the reported data.

IV. CONCLUSION

In summary, pentacene-based OTFTs with the solution-processed HfO_x dielectric have been demonstrated. The solution-processed HfO_x could not only provide a high dielectric constant ($\kappa = 11$) but also has good dielectric strength. Moreover, the rms surface roughness and surface energy (γ_s) on the surface of the HfO_x layer are 1.304 nm and 34.24 $\mathrm{mJ/cm^2}$, respectively, which are compatible to those with additional treatments. The smooth and hydrophobic surface of HfO_x could facilitate the direct deposition of the pentacene film, leading to a high field-effect mobility of 3.8 $\mathrm{cm^2/(V \cdot s)}$. Finally, this letter has shown the low-cost solution process for inorganic material insulators, making them applicable for pentacene-based TFTs.

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